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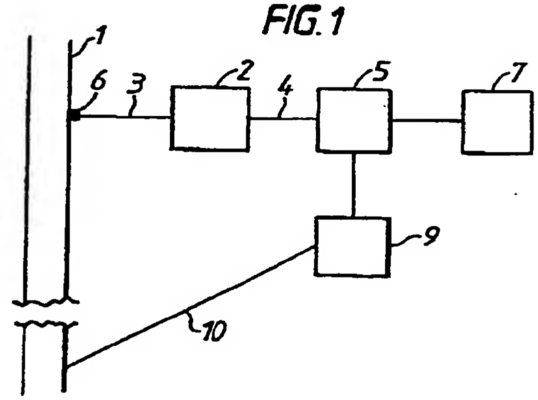
(54) Process control

(57) Method of controlling a process, e.g. a separation, blending or chemical reaction or polymerisation, for which a material X is a feed or a product, in order to keep substantially constant the value V_c of a property P of said product or the product of said process from said feed, or the yield of said process, which method comprises measuring the absorption D_{ix} of said material at more than one wavelength in the region 600-2600nm, comparing signals (i) indicative of said absorptions or a mathematical function thereof with signals (ii) indicative of absorptions D_{im} at the same wavelengths or a mathematical function thereof for at least 2 standards S_m for which the said property or yield has a known value V, at least one of said standards S_{mc} having a value V_c for said property or yield and controlling said process to ensure that said standard S_{mc} or standard(s) S_{mc} is the standard or standards having the smaller or smallest average value of the absolute difference at each wavelength i between the signal for said material and the signal from the standard S_m.

FIG. 1



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Description

This invention relates to a method of controlling by near infra red (NIR) spectroscopy a process which may be a physical or chemical process or separation, in particular involving hydrocarbons, especially in hydrocarbon refineries or for lubricant uses, or chemical processes including polymerisation.

NIR spectroscopy has many advantages over other methods of analysis e.g. in refineries and can cover a large number of repetitive applications accurately, quickly and on line. The NIR region between 800 and 2500nm contains the totality of molecular information in the form of combinations and overtones from polyatomic vibrations, but Mathematical techniques are needed to exploit this information and to calculate the desired parameters. EP-A-285251, 304232, 305090, the disclosure of which is hereby incorporated by reference, describe the use of NIR for determining octane number of a product, or determining yields and/or properties of a product of a chemical process in a refinery or separation process from analysis on the feeds to that process, and yields and/or properties of a product of a blending operation again from analysis on the feed thereto.

At present, numerical methods described for modelling physicochemical properties based on NIR spectra are all of a correlative nature and involve relations of a regressional character between the property(ies) studied. Among these multivariable analyses are multilinear regression (MLR), Principle Component Regression (PLR), Canonic regression, and regression by Partial Least Squares (PLS). In all cases there is sought between the property and the NIR spectrum a relation which may be linear but is usually quadratic or of higher algebraic form involving regression coefficients applied to each absorption. The establishment of any regression requires a progressive calibration, as the approach is empirical and not supported by a theory.

These techniques have disadvantages, the chief of which is the need for establishing a strong correlation between the spectrum and the property, and their difficulty in dealing with positive or negative synergy between components contributing to that property. For example for determining chemical composition e.g. LINA (linear, isoparaffin, Naphthenic, Aromatics) in a hydrocarbon feed to a catalyst reformer, a PLS technique based on the NIR spectra has been described for use. The model works well on the calibration set but the response of the models when pure hydrocarbons are added e.g. cyclohexane is not satisfactory, as the model predicts changes in isoparaffins and naphthenes the reverse of that found experimentally Furthermore there are other practical difficulties, mainly in the need to identify samples of families having the same kind of relation between the spectra and the properties to be modelled. Thus the model may be limited especially with a non linear relation between spectrum and property. Especially when at the edges of the available data the accuracy of the model diminishes. The stability of the model is also a problem, as is the need when adding new standards to do laborious revisions to give the new model, especially when adjusting to a new feedstock for a process; thus testing 6 properties on 4 products leaving a distillation unit requires 24 models, each of which has to be changed for each change of the feed not included in the calibration.

We have discovered a new approach avoiding the above problems with correlations, and regression calculations, and being capable of being expanded automatically with use of a new product of different quality.

The present invention provides a method of controlling a process for which a material X is a feed or a product, in order to keep substantially constant the value V_c of a property P of said product or the product of said process from said feed or yield of said process, which method comprises measuring the absorption D_ix of said material at more than one wavelength in the region 600-2600nm, comparing signals (i) indicative of said absorptions or mathematical functions thereof with signals (ii) indicative of absorptions D_im at the same wavelengths or mathematical functions thereof for at least 2 standards S for which the said property or yield has known value V, and at least one of said standards S_{mc} having said value V_c for said property or yield and controlling said process to ensure that said standard(s) S_{mc} is/are the standard or standards having the smaller or smallest average values of the absolute values of the difference at each wavelength i between the signal for the material and the signal for the standard S_m.

The above method can be performed without regression or correlation techniques, e.g. between the absorption at any wavelength of the material and the property/yield. This method can also be performed without determining said property or yield of said process before controlling the process.

Thus for the performance of the method of the invention, a bank can be prepared in which the NIR spectra are recorded at many wavelengths for a large number of standard materials, together with their properties (or those of products obtained by processes therefrom) determined by alternative techniques e.g. gas chromatography for chemical compositions and yields determined by known methods or viscosities by known mechanical methods. The standards are chosen to cover the area in which the method is to be used, so for octane number determination, a range of gasolines can be chosen of widely varying octane numbers, with e.g. different contents of lead, or other additives such as alkyl ethers and aromatics. For the determination of properties of polyethylenes a range of polyethylenes is chosen of widely varying properties, e.g. with different contents of comonomer, or other properties such as molecular weight. For viscosity determinations for base oils, a range of base oils is chosen of widely varying viscosities. The number of wavelengths chosen may be 2-1000 e.g. 5-200 or 10-20 such as 40-80 especially for oil refining/petrochemical operations as described below, or 5-100 or 10-80 such as 25-65 especially for use with processes which are polymerisation, oligomerisation or an organic reaction in which at least one of the reactant and a product is a functionalised compound,

or 10-80 such as 40-70 especially where material X is a composition comprising part of a lubricating oil fraction from a distillation of oil. The number of standards can be at least 100 or 1000, or 100,000 up to 5 million depending on property(ies) chosen.

The wavelengths chosen may be at regular intervals such as each 1-50 or 10-50 (especially for such processes like polymerisation oligomerisation and reaction as described above) or 15-35nm (or each 1-5nm or each nanometre) or may be at irregular intervals e.g. with intervals of 1-200nm e.g. 1-100 or 1-50 such as 2-50 or 4-50 or 10-60nm, which may be random or chosen because of a change in the shape of the spectral curve at that wavelength e.g. a peak, trough or shoulder or chosen by chemical or statistical criteria such as factor analysis. The wavelengths may be in the region 600-2600nm, such as 800-2600nm, in particular 1500-2600 or 2000-2550nm, especially for oil refining/petrochemical operations as described below or 800-2600 eg 800-2000 especially 1000-1800nm or 2000-2550nm for diene containing gasolines such as ones produced by cracking e.g. steam cracking. The wavenumbers may be in the region 16,600-3840cm^{-1}, e.g. 12,500 to 3840cm^{-1} in particular 6660-3840 or 5000-3900cm^{-1}, or 12500 to 3840 12500-5000 especially 10000-5500 or 5000-3900cm^{-1} especially for oil refining/petrochemical operations as described below; corresponding frequencies in Hertz can be obtained by multiplying these wavenumbers by $3x10^{10}$cm/sec. Wavelengths may also be in the region 600-2500nm, e.g. 900-2500nm such as 1000-2000nm, while the wavenumbers may be 16,600-4000cm^{-1} such as 11000-4000 or 10000-5000cm^{-1}, both in particular for the polymerisation, oligomerisation or organic reactions described above and below. Wavelengths may also be in the region 600-2600nm, e.g. 1000-2500nm but preferably 1500-2600 or 2000-2550nm, while the wavenumbers may be 16,600-3840cm^{-1}, e.g. 10000-4000cm^{-1} e.g. 6660-3840cm^{-1} or 5000-3900cm^{-1}, especially for processes in which material X is a composition comprising part of a lubricating oil fraction from the distillation of oil.

The signals eg absorptions (or derivatives) for the unknown sample are compared with the signals eg absorptions (or derivatives) at the same wavelength of the standards, and those standards chosen having the smallest differences. In the method of this invention, the process is controlled so that at least one of standards chosen is one S_{mc} having the desired value V_c for the property or yield. The absorptions at more than one wavelength may be chosen, e.g. 2-1000 such as 5-100 or 10-20. Other methods of signal processing apart from derivatives such as Fourier transformation may be used in a similar way.

In the method of the invention the standards chosen are those with the smallest average values of the absolute difference at each wavelength i between the signal exemplified by absorption/optical density (or a derivative thereof) D_{ix} for the unknown material and the corresponding signal eg absorption/optical density (or derivative thereof) D_{im} for the standard. The averages may be in respect of the mean value of D_{ix}-D_{im} (whatever its sign i.e. absolute difference), or $(D_{ix}-D_{im})^2$ and may be the simple mean value or the differences may be weighted to take account of the different sensitivity of the absorption to the property at that wavelength or the different sensitivity of the spectrometer at that wavelength. For each standard in the bank of standards for the type of material in question, the average difference is found as described and the standard or standards with the smallest average differences chosen, e.g. at least 1 but preferably at least 2 such as upto 1000 smallest such as 1 (or 2)-100 or 1 (or 2)-20 but is particular 1 (or 2)-10 and especially 2-6 smallest. Advantageously the average differences chosen and hence the standard (or standards) S_m chosen for the property or yield wanted are such that in relation to the unknown material X and each chosen standard S_m the following function is met

$$\frac{i_{xm}}{\Sigma D_{ix}} < \text{experimental error}$$

wherein i_{xm} is the proximity index and is defined by $i^2(xm) = \Sigma(D_{ix}-D_{im})^2$ and the experimental error is in determining said property or yield in the standard. If more than one standard S_{mc} meets the proximity index function then the average of the S_{mc} values usually corresponds to the desired value V_c, especially the arithmetic mean, but optionally with averaging. In a modification of the method of this invention the signals (ii) are indicative of absorptions D_{im} at the same wavelength or a mathematical function thereof of one standard S_{mc} having the known value V_c of said property or yield and controlling said process to ensure that the above function is met.

In order to aid the choice of the appropriate standards, especially in relation to a large number of wavelengths for a complex unknown mixture, it is preferred to limit the choice to those defined by means of a minimal index. For the chosen standard the minimal index is at least the same as the differences between the absorptions of the unknown and the standards. Mathematically, this may be expressed as $i^2ab \leq i^2M$ where iM is the minimal index for the property, and iab is a measure of the deviation (called the proximity index) at all the chosen wavelengths between absorption of the unknown and a chosen standard b. That measure is defined by

$$i(ab)^2 = \Sigma_i (D_{ia}-D_{ib})^2 \qquad (I)$$

where D_{ia} is the optical density (or absorbence) of unknown a at wavelength i (or a derivative thereof e.g. a first, second

or third derivative of that density), and D_{ib} is the optical density (or absorbence) of standard b at that wavelength i (or a derivative thereof e.g. a first, second or third derivative of that density). The value of D_1 is the optical density or the optical density difference with respect to the baseline of the spectrum at that wavelength, or the baseline interpolated between 2 wavelengths on either side thereof. If desired signals corresponding to other mathematical functions of the absorption eg after Fourier transformation or spectral subtraction or division may be used to provide corresponding proximity and Minimal Indices.

If desired instead of the optical density D_i a normalized density W_i may be used where $W_i = D_i/\Sigma D_i$. This normalization avoids errors due to small electronic fluctuations in the apparatus and compensates for small differences in the optical path between the optical cells.. In this case the proximity index is defined by

$$I(ab)^2 = \Sigma_i (W_{ia}-W_{ib})^2 \tag{2}$$

The indices can be weighted as desired for increasing resolution. One approach is to define the indices as follows.

$$I(ab)^m = \Sigma \text{Abs value } (X_{ia}-X_{ib})^m/\sigma_i^{\,n} \tag{3}$$

where X_i is D_i or W_i or a mathematical combination thereof, σ_i is the standard deviation of X for the set of samples considered (at that wavelength) and each of m and n which are the same or different is weighting factor which is positive but can be a whole number or a fraction. Other variants can be used with other weighting factors such as those involving the spectral experimental error e_i, where e_i is the reproducibility of the spectral measurement at wavelength i. The choice between the different options for the weighted indices may be dictated by numerical efficiency.

The reproducibility of the experimental measurements in the standards may be at least 90% or 94% or 95%. The minimal index may be obtained from a reference standard samples set according to the following procedure, hereafter called the Minimal Index Procedure. The NIR spectra for 2 standard samples A and B and their property P e.g. Octane Number, or viscosity e.g. for a polymer, or density e.g. for a lubricating oil fraction are determined. By means of equation (1), (2) or (3), the value of the proximity index i_{ab} is determined via the absorptions at a series of wavelengths; this index is applicable to the difference in properties P_a-P_b called EP_{ab}.

This process is repeated with other pairs of standards c and d, e and f etc to obtain a series of Proximity Indices i_{cd} etc with corresponding property differences EP_{cd} etc. For different values of a parameter L which is greater than the indices i_{ab} etc, the corresponding values of EP_{ab} etc are averaged to give an average EP_{ij} for that value of L; the different values of $EP_{ij}+t\sigma/\sqrt{K}$ are then plotted on a graph against L σ is the accuracy of the property determination and K is the number of pairs of samples for which i_{ab} is inferior to a given L. t is the Student factor at a given level of confidence. The intercept is then measured between the curve obtained and a line usually horizontal which is the reproducibility of the property level at an appropriate confidence interval e.g. 90% or more usually 95%; the abcissa portion of the intercept gives the minimal index i_{min}, which is the minimum value of i_{ab} for which P_a=Pb within the frame of experimental error.

From this minimal index by Procedure 1, the standards can be chosen which have values of $i^2_{ab} \le i^2_{min}$ where in this case a is the unknown and b is a standard, as in this case the difference between Property a and Property b is less than or equal to $\sigma\sqrt{2}$, where σ is the experimental error in measuring the property. Then if the standard meeting this requirement is S_{mc} with property or yield value V_c, the process is under control, but if a different standard is nearest to the unknown then process needs adjustment as described below.

The process may be controlled to keep substantially constant more than one Property or yield at once, e.g. at least 2, such as 1-30 e.g. 2-10 properties at once. Each property of the standards has a particular unweighted, minimal index, which may lie in the region 0-10^{-10} e.g. 10^{-1} to 10^{-9} or 10^{-2} to 10^{-8}, in particular 10^{-7} (or 5×10^{-7}) to 5×10^{-4} for Minimal Indices derived from absorbancies; corresponding Minimal Indices may be obtained for other signals/functions. If the Minimal Index chosen is the smallest for all the properties desired, then the same one may be used for all the properties and the standards chosen will be suitable for all the properties. The Minimal Index for each property may be used separately, with different numbers of standards chosen for each property (assuming different Minimal Indices). If desired the same Minimal Index may be used, which is not the smallest, resulting in some of the chosen standards (with a higher Minimal Index) giving some properties of high accuracy and some (with a lower Minimal Index) giving some properties of less high accuracy.

The value of the property or yield to be controlled may be of the sample being analyzed or a product obtained from that sample e.g. a product of blending, cracking, separating or polymerising the sample, as the property value obtained is derived from the standards, and they will have been determined as needed for the eventual use. Our EP304232 and 305090 referred to above describes such techniques when applied to use of NIR with correlation to blending, separating or cracking operation; the same principles apply in the present method.

If the density of the standards in the data bank is sufficient to have $i^2ab \le i^2$ min as is usually the case, the above procedure is very satisfactory. But there are occasions when the bank is incomplete, because of shortage of data of properties in a particular area i.e. a low density of standards or the sensitivity of the property to changes in absorption

is so small, that a very small Minimal Index is required and there may be few standards with proximity indices meeting it. It is possible simply choose a larger Minimal Index with e.g. 1-5 times such as 1.5-2 times the Minimal Index; the results may be less accurate than those from a smaller minimal index.

However, a more accurate approach with a low density of standards involves a special densification process of Procedure 2, in which random or semi random densification of the neighbourhood of the unknown is achieved by generation of synthetic standards, based on standards already in the bank. Each new synthetic standard may be obtained from combinations of standards taken at random from the bank but preferably it is obtained from the other standards by the constraint of choosing only a mixture of N standards for which

$$(Min)C_j - u_j \leq C_{ij} \leq (Max)C_j + u_j \quad (4)$$

and

$$\Sigma C_{ij} = 1 \quad (5)$$

where C_{ij} is the fraction of component j in the sample $_i$.

Min C_j is the minimum amount of $_j$ in the initial calibration mixture i.e. standards in the bank or in the samples for which the method is to be used, and
Max C_j is the maximum amount of $_j$ in the initial calibration mixture i.e. standards in the bank or in the samples for which the method is to be used, and
uj is usually between 1 and 0.01 or 1 and 0.05 preferably between 0.5 and 0.1 and can be fixed for each property.

The constraints over the choice of such mixtures of N standards can also be equally fixed in the spectral area from which the samples will be drawn in order to remain in the areas of similar chemical nature.

The number of samples effectively drawn into the bank in this densification can be of several thousand generally 1000-2000. The calculation time is extended without significant deterioration in the results. If no further neighbours are found, the trawl of new samples drawn in is enlarged.

The spectrum of each mixture is calculated by the combination of the spectra of the standards used according to the formula

$$S_{Mi} = \Sigma C_{ij} X S_j \quad (6)$$

where S_j is the spectrum in the mixture of component $_j$ in the calibration matrix.

The properties of each mixture PMi can be calculated by a generally linear combination of the properties of the standards according to the formula

$$P_{Mi} = Z C_{ij} X P_j \quad (7)$$

where P_j is the property of component j

In the case of non linear additive properties, appropriate mixing factors can be applied e.g. by blending factors or similar for density and viscosity.

Having obtained the spectrum and the properties of the synthetic mixtures, these can be used as "standards" to help control the process by keeping the properties constant in the same way as a conventional standard.

Instead of using either of the two above approaches, 1-7, a third type Procedure 3 may be used as follows. The Q nearest samples to unknown X can be found from a selection from the bank samples for which the proximity index to the unknown sample is (V) X i_{min}) where v is $0.1 < v < 10$, (8) preferably $0.5 < v < 2$ or $1 \leq v \leq 5$. Then by the method of least squares is found a generally linear combination of the standard products, which are the Q nearest samples, to reproduce the spectrum of X according to the equation.

$$S_x = \Sigma C_R X S_r \quad (9)$$

where C_r is the coefficient for sample R in the total Q and S_R is the spectrum of sample R. The coefficient C_R which can be normalized to $C_R = 1$ or not and/or optimized by the least squares route, allows an estimation of the property P_x according to the equation.

$$P_x = Z C_R X P_R \quad (10)$$

where P_R is the property of sample R.

The eventual size of the estimation error can be derived by application of Gaussian theory, also called the propagation error (see Eq.10).

The above third approach can only be applied if the product X is situated inside the maximum extension of the standard products defined by equation (8) i.e. within the range of bank samples defined in equation (8). If this is not the case, X is outside the field of the actual bank of products and escapes from the area of knowledge of the method into the area of learning.

The densification process described in relation to equations 4-7, or 9 or 10 is usually applied to the method of the invention involving no correlation or regression techniques. However, if desired the densification process may be applied to increase the number of "standards" for consideration in an NIR analytical technique involving the correlation on regression techniques as described above e.g. MLR. The present invention also provides a method for adding an extra synthetic standard to a bank of known standards, each of which relates at least one absorption in the 600-2600nm region (or a signal indicative thereof or of a mathematical function of said absorption eg a derivative thereof) of a known material to a known property related to that material, which method comprises choosing from the bank at least 2 standards for which equations 4 and 5 above are met, considering mixing the chosen standards in at least one proportion to produce at least one mixture for use as a synthetic standard, and estimating the spectrum and property/yield of said mixture according to equation 6 and 7 respectively.

The spectrum and property/yield of each "mixture" can then be added to the bank and used to develop models through the known correlation/regression approach, e.g. as described in the above mentioned patents.

As explained above if the nearest standard to the unknown is not one having the value V_c for the property or yield, or having a value V for said property or yield within ± 10%, e.g. ± 5% or ± 1% of said value V_c, or if the function $i_{xm}/\Sigma D_{ix}$ is greater than the experimental error, especially more than 10%, 5% or 1% greater, then the process has deviated and needs adjustment, e.g. by changing one of the parameters of the process e.g. reaction conditions such as temperature, pressure, or amount/nature of catalyst for a reaction, or proportions or nature of the feeds in the case of a blending or reaction.

The method of the invention may be applied from the spectrum of a material to control the process to keep substantially constant the value of at least one physical, chemical, physicochemical and/or rheological property of that material, which may be a product of a chemical or physical or separation process, or which may be a feed to such a process, or the method can be used to control the process to keep substantially constant the value of at least one of said properties of a product of that process from the spectrum of at least one feed to that process, or to keep substantially constant the yield of at least one product of that process. Each of the feed (or feeds) or products to the process may be a solid liquid or gas preferably at least one feed or product is a liquid.

Thus the method may be used to control a process in relation to at least one feed or product used in or obtained by an industrial process of the refining of oil and/or in petrochemical operations. The process may be a hydrocarbon conversion or separation process, preferably a reforming or catalytic cracking or hydrotreatment process or distillation or blending. In particular it may be used to control a process to keep substantially constant at least one property of a feed and/or at least one property and/or yield of product from a number of different processes such as processes for separating petroleum products such as atmospheric distillation vacuum distillation or separation by distillation, under pressure greater than atmospheric, as well as thermal or catalytic conversion, with or without partial or total hydrogenation, of a petroleum product, such as catalytic cracking e.g. fluid catalytic cracking (FCC), hydrocracking, reforming, isomerization, selective hydrogenation, viscoreduction or alkylation.

Of particular value is the use of the method in blending operations involving control of the value of at least one property of a blend of liquid hydrocarbons (optionally with other additives such as alkyl ethers), this method including or not the determination for each constituent of the blend of a blend index for the property considered. In this method as applied to blending, the blend indices can be obtained simply by calculation and without the need for preparation of standard physical mixtures other than those contained in the databank. The blend indices can be combined linearly or non linearly within the fields of stability to determine from the value of this combination a value for at least one property of the blend obtained. The blend may be made by mixing at least 2 of butane, hydrogenated steamcracked gasoline, isomerate, reformate, MTBE or TAME, FCC derived gasoline.

Examples of properties of materials in processes controlled by the method of the invention include the following: for automobile fuels/gasolines, at least one of the Research Octane Number (RON), Motor Octane Number (MON) and/or their arithmetic mean, with or without lead additive and/or the methyl tert, butyl ether or methyl isoamyl ether and/or benzene content:

For automobile fuels/gasolines, at least one of the vapour pressure, density, volatility, distillation curve, e.g. percentage distilled at 70°C and/or 100°C, oxygen content or benzene or sulphur content, chemical composition and/or gum content e.g. expressed in mg/100ml, and/or susceptibility to lead (these properties are particularly determined for use in blending operations):

For diesel fuels or gas oils, at least one of the cetane number (e.g. motor measured), cetane index, cloud point, "discharge point", filterability, distillation curve, density e.g. at 15°C, flash point, viscosity e.g. at 40°C, chemical composition, sensitivity to additives and percentage of sulphur;

For distillation products from crude oil e.g. under atmospheric pressure at least one of the density, percentage of sulphur, viscosity at 100°C, distillation curve, paraffin content, residual carbon content or Conradson carbon content, naphtha content, flash point for petrol, cloud point for gas oil e.g. light gas oil and/or viscosity at 100°C and/or sulphur content for atmospheric residues, and yield for at least one of the cuts, gasoline (bp 38-95°C), benzine (bp 95-149°C) naphtha bp 149-175°C, jet fuel bp 175-232°C, light gas oil bp 232-342°C, heavy gas oil bp 342-369°C, and atmospheric residue greater than 369°C.

For at least one of a feed or a product of a process of a catalytic cracking e.g. FCC process, at least one of the density, percentage of sulphur, aniline point, gas oil index, gasoline index, viscosity at 100°C, refractive index at 20°C and/or 60°C, molecular weight, distillation temperature e.g. 50% distillation temperature, percentage of aromatic carbon, content of total nitrogen and factors characterizing the suitability of the feed for the cracking e.g. KUOP, crackability factor, cokability factor, and yield e.g. of gas, gasoline, gas oil or residue. Thus there may be determined the yields and/or properties of the different products obtained by distillation of the cracked products, such as RON and/or MON, clear or leaded for the gasoline cut and the viscosity at 100°C for the distillation residue.

For at least one of a product or a feed of a catalytic reforming process, at least one of the density, distillation temperature and/or chemical composition (expressed as a percentage) of saturated linear hydrocarbon, isoparaffins, naphthenes, aromatics and olefins.

For at least one of a product or a feed of a process of hydrogenating gasoline at least one of the density, distillation temperature, RON and/or MON, clear or leaded vapour pressure, volatility, chemical composition (expressed as a percentage) of saturated linear hydrocarbons, isoparaffins, naphthenes, aromatics e.g. benzene, and mono/di substituted benzenes, olefins e.g. cyclic and non cyclic olefins, diolefins, the maleic anhydride index, and yield e.g. of at least one of the products obtained.

The method of the invention may also be used with chemical reactions in which at least one product is a hydrocarbon, and none of the feeds or products contains an element other than carbon or hydrogen. The hydrocarbon which may be gaseous or liquid at 25°C. Such reactions may involve as feed or product at least one olefin or acetylene e.g. linear or branched, aliphatic or cycloaliphatic olefin with an internal or external ethylenic unsaturation, preferably of 2-20 carbons especially 2-8 carbons for alkenes or alkynes (such as ethylene, propylene, butene 1 or 2, isobutene, isopentene) or acerylene, and 5-8 carbons for cycloalkenes e.g. cyclohexene. The feed or product may also be an aromatic hydrocarbon e.g. benzene or naphthalene, optionally substituted by at least one (e.g. 1-3) alkyl or alkenyl group e.g. of 1-20 carbons, such as 1-6 carbons, especially methyl, ethyl or isopropyl; examples are benzene, toluene xylene, cumene and styrene. The feed or product may also be a non aromatic hydrocarbon, e.g. linear or branched aliphatic or cycloaliphatic with e.g. 1-20 or 5-8 carbons respectively, preferably 1-6 carbons and 6 or 7 carbons respectively, examples are methane, ethane, propane, n-butane, isobutane, and cyclohexane. The feed or product may also be a diene, conjugated or unconjugated, aliphatic or cycloaliphatic with e.g. 4-20 carbons or 6-20 carbons respectively; examples are butadiene and isoprene and cyclohexadiene. Examples of the reactions are hydrogenation (e.g. butadiene to butene-1 or 2 or cyclohexene to cyclohexane) dehydrogenation (e.g. ethane to ethylene or ethyl benzene to styrene), isomerisation (e.g. butene-1 or -2 to isobutene, or pentene-1 to isopentene) alkylation (e.g. benzene with ethylene to form ethylbenzene and/or styrene, or isobutene with butane to form iso octane), and cracking.

In addition to the use in petrochemical operations, the method is of wider application and may be applied in the pharmaceutical industry such as the production of pharmaceutically active compounds for use as medicines e.g. by fermentation, and in the perfumery industry for making perfumes and fragances, especially in their blending and control thereof. The method may also be used in the food industry e.g. in brewing to control fermentation processes, in fermentation to make wine and quality control thereof, and control of food production e.g. sugar and water content in fruit juice and in control of maturing processes for fruits and vegetables. In each case the method may be applied to keep substantially constant the property of the sample tested or product from that sample e.g. a fermentation or blended product preferably on line and especially with continuous feed back from the results to control the production process.

The known correlative techniques for modelling physicochemical properties based on NIR spectra have disadvantages, the chief of which is the need for establishing a strong correlation between the spectrum and the property, and their difficulty in dealing with positive or negative synergy between components contributing to that property. In the case of high density polyethylene one multi linear regression model in respect of density gives a coefficient of correlation that can on occasion be insufficiently high, so as to give problems in a polymerization process based on it.

The method of the invention can avoid the above problems with correlations, and regression calculations.

The present invention also provides a control method, in which the process controlled is at least one of a polymerization, an oligomerization or an organic reaction in which at least one of the reactant and a product is a functionalized compound. The above method can be performed without regression or correlation techniques, e.g. between the absorption at any wavelength of the material and the property/yield.

The method of the present invention is applicable to chemical reactions, which may be polymerisations or oligomerisations, or alternatively reactions in which at least one of a reactant and a product is a functionalised compound. In the chemical reactions each of the feeds and the products may be a solid, liquid or gas, preferably all the feeds are liquids and/or gases, and preferably all the products are liquids and/or solids, especially liquids.

Examples of polymerisations are condensation and addition polymerisation. Condensation polymerisations may produce thermoset polymers, such as phenolic novolac or resole resins curing with or without curing agents like hexamine, or polyurethanes, or thermoplastic polymers such as polyamides, e.g. polylactams such as Nylon-6 and polymers from polyamines and polycarboxylic acids e.g. poly hexamethylene adipate, and polyesters, such as those from diols e.g. aliphatic diols and organo di carboxylic acids e.g. aromatic or aryl bis (alkylene) dicarboxylic acids, such as poly ethylene terephthalate. Addition polymerisations tend to produce thermoplastic polymers, and may be thermal or free radical or catalysed reactions e.g. with Bronsted or proton acids or metals, especially transition metals. Examples of such polymerisations are those involving polymerisation at an olefinic double bond or ring opening of an epoxide or episulphide. The olefinic double bond is preferably a vinyl group CH_2=C- and may be in a hydrocarbon e.g. an olefin especially an alkene such as one of 2-12 carbons especially ethylene alone or mixed with at least one alpha olefin of 3-12 carbons (especially in amount of 0.5-30% by weight based on total olefins) such as propylene, butene-1, 4-methylpentene-1, hexene-1, octene-1 or styrene; copolymers of such olefinic hydrocarbons, especially ethylene, with non hydrocarbon comonomers e.g. esters with olefinic groups such as vinyl esters e.g. vinyl acetate or alkyl(meth)acrylate or vinyl chloride may also be made. Addition polymerisation of iso olefins e.g. of 4-8 carbons such as isobutene alone or with other comonomers such as butadiene is included, as in addition polymerisation of olefinic non hydrocarbon monomers such as vinyl esters e.g. of 3-20 carbons especially 4-10 carbons such as vinyl acetate and propionate, and alkyl(meth)acrylates wherein the alkyl group has 1-20 carbons, especially 1-4 carbons for solid polymers e.g. polymethyl methacrylate, and 4-20 carbons for polymers for use as pour point depressants and VI improvers e.g. polydodecyl acrylate and methacrylate and copolymers with 2-10 monomers of different alkyl chain lengths. Vinyl chloride homopolymers and copolymers e.g. with vinylidene chloride may also be made.

The method may also be used for ring opening reactions such as reactions of epoxides, episulphides or cyclic imines with organic compounds containing at least one active hydrogen such as compounds with at least one OH, NH or SH group, such as alcohols, phenols, primary or secondary amines or thiols. Alcohols e.g. of 1-30 carbons such as 2-6 carbons (e.g. butanol) especially alkanols or cycloalkanols are preferred. The epoxide is usually of 2-8 carbons e.g. ethylene oxide, propylene oxide, butylene oxide or cyclohexane oxide, while the episulphide and cyclic imines are preferably the corresponding analogues e.g. ethylene imine and ethylene sulphide.

In the case of polymerisation the method may be used to keep substantially constant the properties of the polymer made from the NIR spectrum of the feedstock (under constant conditions) or from the NIR spectrum of the product. Examples of properties are number and weight average molecular weights, and the molecular weight distribution, viscosity e.g. at 100°C, fluidity index, density, and chemical composition e.g. percentage of at least one monomer or comonomer in the polymer percentage of unsaturation e.g. ethylenic type, or side chain grouping, e.g. methyl, crystallinity, rigidity, flow parameters, draw strength at the flow threshold, free cracking resistance and shock resistance. In addition for polyisobutenes, the property may also be content of butene-1, and light and heavy polyisobutenes and unsaturation expressed in groups per litre and maleinisation index (or succinylation ratio) (sensitivity to Diels Alder reactions) as well as particular types of unsaturation e.g. vinylidene CH_2=C- VIN, tri (CH_3-C(CH_3)=CH<) TRII, tri 2 (TRI2) (CH_3-CH=C-) TRITOT (R-CH=C<), TETRA (>C=C<). For polyolefins e.g. polyethylene, other properties include percentage of comonomer, volatile compounds and degree of conversion. For polyalkylenoxylated compounds e.g. ethylene oxide condensates e.g. with alcohols, the method may be used to monitor the degree of conversion or the amount of alkylene oxide consumed, as well as the quality of the product e.g. content of groups derived from at least one epoxide or the distribution of those groups in the polymer chain, the product weight and number average molecular weight and its distribution, proportions of low and high molecular weight products (e.g. 150-600 or 600-15000 such as 5000-12000 respectively) Hydroxyl index (or mean number of hydroxyl groups per molecule), percentage of primary secondary and tertiary hydroxyl groups, allylic or propylenic type unsaturation, or impurity content. The method is of especial value in the polymerisation of ethylene alone or with at least one alpha olefin as described above. The process is usually catalysed by at least one transition metal catalyst especially of Group IVA, VA or VIA, of the Periodic Table, such as titanium, zirconium, vanadium and/or chromium. The catalysts may be organometallic (including II complexes), especially with the above transition metals, and may be in the presence of at least one organo aluminium cocatalyst as in Zeigler Natta catalysts. Non organometallic catalysts such as chromium oxide may be used. The catalyst may be unsupported or supported e.g. on silica and/or alumina.

The method may also be applied to organic chemical processes, which are not polymerisations (including oligomerisation); thus processes involving only monomeric starting materials and products are suitable. In particular these include processes in which at least one of a reactant and a product is a functionalised compound i.e. is not a hydrocarbon but contains at least one functional group, e.g. with at least one atom other than carbon and hydrogen, in particular at least one oxygen, nitrogen, sulphur, phosphorus, or halogen e.g. chlorine, bromine, iodine or fluorine atom, especially 1-3 such atoms in the compound. The functional group may be an alcohol, phenol, thiol, primary secondary or tertiary amine, aldehyde, ketone, ester, acid, amide, nitrile or ether or sulphide, or aromatic or aliphatic halide.

In particular the process may be a hydration such as an olefin to an alcohol (e.g. ethylene or propylene to ethanol or isopropanol respectively) dehydration such as an alcohol to an olefin (e.g. tert butanol to isobutene) etherification such as reaction of an alcohol or phenol with an olefin (e.g. tert butanol with isobutene to form Methyl tert butyl ether)

or reaction of an olefin with water (e.g. ethylene to diethyl ether), esterification such as reaction of a carboxylic acid (or derivative thereof e.g. acid chloride) with an alcohol e.g. alkanol of 1-20 carbons) or with an olefin (e.g. ethylene, propylene or n or isobutene), such as reaction of acetic acid with ethylene to form ethyl acetate or with dehydrogenation) vinyl acetate. The process may also be an oxidation e.g. an alcohol or aldehyde to an acid such as methanol to formic acid, or a hydrocarbon to an alcohol or ketone or an acid e.g. naphtha to acetic acid or methane to formic acid or cumene to acetone and phenol, an ammoxidation e.g. an aliphatic substituted olefin (with optionally 3-6 carbons) to a nitrile such as propylene to acrylonitrile, or a carbonylation of an olefin or an alcohol to form a carboxylic acid and/or anhydride, such as the reaction of methanol with carbon monoxide to form acetic acid and/or anhydride.

The method may also be applied when the material X is a composition comprising part of a lubricating oil faction obtainable from a distillation of oil e.g. a vacuum distillation of oil.

This embodiment of the method of the present invention is applicable to various petroleum hydrocarbon fractions, which comprise part (and only part) of a lubricating oil fraction e.g. from a vacuum distillation of oil after removal of materials boiling above 370°C (under atmospheric pressure). Such fractions include the partly purified lube cut from the distillation, e.g. after at least one of the steps of dewaxing and dearomatizing and preferably both, (as in lube base oil) and the partly purified vacuum distillation residue e.g. after at least one of the steps of deasphalting, dewaxing and dearomatizing, and preferably all 3 (as in bright stock). Such fractions also include the aromatic extract of the lube oil cut or distillation residue, or a wax separated therefrom.

The method is preferably applied to control of production of lube base oils or bright stock. The base oil may be a 100-600 neutral or solvent or BS oil e.g. 100, 150, 200, 300, 400 or 500 neutral oil or BS solvent. It may have at least one of and preferably all of the following properties a density at 15°C of 0.80-0.95kg/l e.g. 0.85-0/92kg/l, a kinematic viscosity at 40°C of 10-1000cSt e.g. 15-700cSt, and at 100°C of 0.5-50cSt e.g. 1-40cSt, a Flash Point of 180°C min e.g. 190°C min, a pour point of 0°C maximum e.g. -5°C or -7°C maximum and a Viscosity Index of 80min e.g. 90min. The base oil may be present alone, or may be mixed with the aromatic extract as in process oils, which may have at least one of, and preferably all of the following properties, a density at 15°C of 0.95-1.10kg/l, e.g. 0.97-1.06kg/l, a Kinematic Viscosity at 40°C of at least 30cSt e.g. at least 37cSt, and at 100°C of at most 50cSt e.g. at most 45cSt and a Flash Point of at least 185°C e.g. 190°C min. The base oil may also be present mixed with at least one wax e.g. in amount of, 0-50% such as 1-40% or 15-35% by weight as in "slack wax", the mixture of oil and solid wax separated in the dewaxing step, or waxes as in the residue from the dearomatization step.

The base oil may also be mixed with at least one non hydrocarbon additive to boost its effectiveness for lubricant use. Types of additives which may each be present in amounts of 0.01-10% by weight (based on the weight of base oil) e.g. 0.1-1% are (i) detergents/dispersants such as alkyl phenates and/or alkyl aryl sulphonates (ii) antioxidants such as phenol derivatives, (iii) viscosity index improvers and pour point depressants, such as alkyl poly(meth)acrylate homo and especially copolymers, styrene butadiene polymers and polyisobutylene (iv) anti corrosives, such as sulphur compounds, zinc sulphophosphates and dithiophosphates, and (v) solid or liquid lubricity additives, such as graphite, molybdenum disulphide and silicones.

The method may also be applied to the aromatic extract resulting from the extraction of aromatics (e.g. with furfural) from the lube cut of the vacuum distillate or the deasphalted vacuum residue. This aromatic extract is different from the base oil as it contains a much higher amount of aromatics, such as benzene, toluene and xylenes, and higher molecular weight aromatics e.g. of at least 30 carbons than the base oil. The aromatic extract may be used alone or mixed with an amount of base oil to form process oil.

The method may also be applied to solid or liquid paraffins or waxes e.g. as separated in a dewaxing step from the lube cut or the deasphalted residue. The wax may be mixed with base oil as in slack wax, or substantially free of base oil and may then if desired be further purified to produce a paraffin. Waxes may be used industrially while paraffins may be used for food and cosmetic uses.

The method is preferably applied for process control in a part of a refinery producing lubricants and by products therefrom.

Examples of properties whose values can be kept substantially constant for the various materials are as follows. Where the material is a base oil (or formulated oil) the property may be at least one of the density, sulphur content, Flash Point, Flow Point, kinematic viscosity at 40°C and at 100°C, Viscosity Index, aromatic carbon content, Polycyclic Aromatic hydrocarbon content, nitrogen base content, and inflammability according to Pensky Martens °C. When the material is a crude paraffin or slack wax, the property may be at least one of the density, viscosity e.g. at 40°C or 100°C and oil content. When the material is a process oil, the property may be at least one of the density, sulphur content, Polycyclic Aromatic hydrocarbon content, viscosity e.g. at 40°C or 100°C and the Flash Point e.g. Cleveland Flash Point.

In each of the above processes the control may be performed and notice taken of any deviations by adjusting the parameters of the process e.g. flow rates proportion or nature of feed(s) (e.g. via operation of control valves) and/or temperature/pressure etc to bring the property or yield back to the desired figure. This control of the process, which may be a blending, separation or chemical e.g. polymerisation process, is usually performed with a micro computer which is linked to the spectrometer and also performs the search for the standards Sm. The inline control of the process is very

efficient and very fast.

The present invention also provides an apparatus suitable for carrying out the method of the invention comprising an infra red spectrometer and a computer wherein the infra red spectrometer is linked to the computer programmed in such manner to determine the nearest standard, and this in turn is linked to a control means to adjust the process in response to any deviations when S_{mc} is not the nearest standard. The spectrometer is suitable for measuring spectra in at least partly in the 600-2600nm wavelength range and can be linked to a signal processing device to allow numerical treatment of the spectrum, preferably by Fourier Transformation. The spectrometer receives at least one signal from a vessel containing product or from a feed or product line. The information obtained can be used as an information vector for the computer which is programmed to determine the nearest standard e.g. via calculations on the proximity indices in relation to standards. Conveniently in relation to the process, the computer may be used in a closed loop feed back or feed forward control system for controlling processing equipment e.g. changing the process parameters in response to variations in the nearest standard from measurement of more than one absorptions in the NIR spectrum of the product and/or feed.

The present invention also provides a computer programmed to perform the method of the invention. The apparatus for use with the former method of the invention comprises an NIR spectrometer receiving at least one signal from a feed or product line in said process and being coupled to a computer to effect continuous measurement of the spectra of the feed and/or product and provide feed back or feed forward control of the process. The present invention also provides a computer implemented method for a system including a spectrometer linked to a process line containing a material X, a computer linked to the spectrometer, and a controller linked to the computer and the process line, the computer including databanks having stored therein signals indicative of absorptions of standard materials (or mathematical functions thereof) and corresponding properties of said materials or products of said process for which X is a feed, or yield of said process, the method comprises steps of:

measuring absorption at more than one wavelength in the region 600-2600nm at the process line and producing absorption signals (or mathematical functions eg derivatives thereof) by the spectrometer in accordance therewith;
accessing the databanks of the computer in accordance with the absorption signals (or functions thereof);
comparing, by the computer, the absorption signals (or functions thereof) to the signals (or functions thereof) of the standard materials stored in the databanks;
choosing at least one standard based on the comparing, said standard having the smallest average value of the absolute difference at each wavelength i between the signal for the absorption (or function thereof) for the material and the signal (or function thereof) for the standards; and
controlling said process directly in accordance with the outputted standard, to ensure standard S_{mc} is the one with the smallest average value.

The benefits of invention allow improvements in control of processes involving modelling with the following areas, identification and classification of novel products, simultaneous control of all of the properties on a sample without the need for generating different models for each. The method of the invention overcomes the difficulties with the classical regressional approach, in particular avoiding all difficulties with numerical stability of the models.

The method also allows an extension of the field of application of the method without the need to rewrite the model, apart from the need to integrate the new samples which are inside or outside the previous field of validity of the method. This possibility of automatic learning, which is not possessed by traditional regression techniques, is a decisive advantage in the framework of continuous inline industrial control processes, because it allows the return of the industrial plant operations to the model in a certain and rapid manner in a minimum time and with all the properties considered in the model. In contrast classical regression methods would necessitate the redevelopment of all the models, which is long and laborious without being able to guarantee the result of the new model obtained, because a new validation period is necessary; in addition during the redevelopment of the model any commercial use e.g. in a refinery of the model is very limited. Furthermore, the method of invention allows equally the easy extension to a number of properties, which are simply incorporated into the known bank.

This remarkable possibility is true not only for control of processes with conventional properties such as physical chemical and/or rheological properties, but also for complex ones (such as octane number). Also it is possible to quantify by the process the response or susceptibility to lead of automobile fuels as well as the response to additives such as nitrates, of fuels used in diesel engines. The methods of the invention equally allow application of the models from one apparatus to another and from one spectral region to another, where conventional regressive method cannot give satisfactory solutions. This apparatus portability is made possible by the fact that the differences between different spectra are the same in one apparatus as another, for the same type of spectrometer being considered (e.g. network scatter, Fourier transform, accousto optical system AOTS, diode array etc). This portability between spectral regions depends on the fact that as the spectral regions are intercorrelated, the relations between the spectra are maintained between one another.

The invention is illustrated in the accompanying Figures in which :

Figure 1 represents a schematic diagram showing apparatus for use in the invention;

Figure 2 represents a schematic block flow diagram for the method of the invention.

In Figure 1, an optical fibre 3 links a spectrometer 2 and a probe 6 in or at process line 1. The spectrophotometer 2 produces absorbance signals at more than 1 wavelength, which signals as such (or after mathematical treatment to form e.g. derivative signals) are passed via line 4 to computer 5, where the signals as such or after conversion e.g. to one or more derivative signals, are used to enable the computer to access the databank 7 of standard signals eg absorptions and properties/yields therein. The signals are compared to those of one or more standard absorption(s) as described above. The output of the computer 5 is in the form of a signal which is used to control the process involved with the product in line 1, ie for which line 1 is a feed or a product line; in this case the computer 5 is linked to and instructs the controller 9 which, via 10, controls that process eg. via valves/temperature and/or pressure controls in line 1 or in relation to line 1. By this means the property of material in line 1 or yield or property of product of the process from that material can be kept substantially constant without the need to determine that property or yield.

In Figure 2, the initial operation 11 is to measure the absorption of the unknown, after which in the second step 12, the absorptions are compared to absorptions in spectra of standards, and in the third step 13, the spectra of the standards Sm are chosen according to criteria described above, and then in step 14, if the standard S_m chosen is not S_{mc}, in step 15 the process involving the unknown is adjusted to keep the standard chosen to be S_{mc} and hence to keep the value of the property or yield substantially constant.

The invention is illustrated in the following Examples in which the Minimal Index is calculated according to the Minimal Index Procedure described above. Mathematically the steps concerned are as follows.

For each couple of standard samples i, j, the Proximity Index i_{ij} is determined from the NIR spectra by use of equation 1, 2, or 3 and the properties are measured. For each Proximity Index is calculated the absolute difference EP_{ij} between the properties of the samples. The Minimal Index for property P is obtained from the average (EM_pL) of EP_{ij} for different values of L when L ≥ij. Thus the $EM_p(L) = 1/K\ \Sigma_i\ \Sigma_j\ EP_{ij}$ for each of K samples for which $i_{ij} \leq L$.

$EMp(L)+t\sigma(M)$ is plotted against the proximity index and in addition there is plotted the reproducibility of the standard method at a given level of confidence, as defined in the Minimal Index Procedure above. The intercept of the curve from EMpL and the reproducibility give the upper limit i.e. the Minimal Index.

For the Examples the data is expressed in Tables in a form as shown below in For each Proximity Index is calculated the absolute difference EP_{ij} between the which the data is as follows.

		Absorption				
		Weighting	Unknown	Estimated	Standard A	Standard B
Proximity Index						
Wavelength λ						
cm^{-1}	nm					
Property I						
Property j						
Property m						

The wavelengths chosen are shown in columns 1 and 2.

Column 3 gives the weight loading associated with each wavelength for the proximity index for the standards; I denotes no loading.

Column 4 shows for the unknown sample the absorption at the various wavelengths and at the bottom the properties of that sample determined by standard methods.

Column 5 shows for the unknown sample the estimated values of the properties and the absorptions using the method of the invention based on the properties and absorptions of the chosen standards.

Columns 6, 7 etc show the values of the absorptions and properties for the standards chosen from the bank. Line 2 gives the value of the proximity index between the unknown sample and each of the chosen standards.

Example 1

(a) Production of an Unleaded Mixed Fuel from 6 Components

A target SUPER98 superfuel of the properties given in column 3 of Table 1a1, was to be obtained by mixing the remains of a tank of finished gasoline with 5 components, butane, hydrogenated steamcracked gasoline HEN, isomerate ISOM, reformate (REF) and MTBE in volume proportions 19.30%, 4.10%, 31.70%, 32.10%, 7.2% and 5.6% respectively. NIR absorptions at 4800-4000cm^{-1} measured with a Fourier Transform spectrometer were measured, with a base line taken at 4780cm^{-1} and absorbances normalized. Results are in Table 1a.

The 6 components were then mixed in the desired proportions, the mixing controlled by the method of the invention applied to the spectra from the components present (see Results in Table 1b). In the comparison with the bank of standards, the Minimum Index was 1×10^{-4}. 3 standards 1D, 1E, 1F were found with suitable proximity indices for which standards the average value of the properties corresponded to V_c, the desired value of the property of the target fuel. The blending process was controlled to maintain the 3 standards 1D, 1E, 1F as those with the suitable proximity indices and hence keep substantially constant the properties of the superfuel. For double checking the properties of the blend made and the properties estimated by averaging those from the standards 1D, 1E and 1F were compared; the differences are very small and in the area of reproducibility of the standard methods.

TABLE 1a

NIR Spectra of Unleaded mixed fuel and base fuel and additives

		SUPER FUEL	BASE FUEL	BUTANE	HEN	ISOM	MTBE	REF
λ (cm-1)	λ (nm)							
4720	2119	0,0013833	0,0013286	0,00036614	0,0048746	0,00045176	0,00039505	0,0017899
4670	2141	0,015401	0,015698	0,00059139	0,035929	0,0018107	0,00079685	0,02742
4640	2155	0,014458	0,014786	0,0015483	0,03355	0,0020854	0,0019907	0,026581
4615	2167	0,021629	0,02193	0,002432	0,048472	0,0033767	0,0033645	0,035613
4585	2181	0,013173	0,013556	0,0039046	0,026822	0,0032492	0,0043356	0,026327
4485	2230	0,010699	0,010705	0,013766	0,01651	0,0057573	0,013241	0,012712
4460	2242	0,015318	0,015646	0,016717	0,018858	0,010108	0,027911	0,0181
4385	2281	0,094023	0,094638	0,10437	0,081125	0,095255	0,13276	0,084676
4332	2308	0,12974	0,13083	0,14701	0,094876	0,1474	0,18122	0,11297
4305	2323	0,10626	0,10476	0,12279	0,093425	0,11981	0,063885	0,10927
4260	2347	0,10094	0,098881	0,11439	0,088133	0,11705	0,074657	0,090487
4210	2375	0,065672	0,065902	0,074313	0,054295	0,072316	0,091152	0,058007
4170	2398	0,065289	0,065063	0,057805	0,049811	0,074797	0,095725	0,05451
4135	2418	0,069147	0,068664	0,079862	0,046235	0,085847	0,083448	0,049256
4105	2436	0,068641	0,067702	0,089697	0,050826	0,082082	0,06768	0,053229
4060	2463	0,10677	0,10794	0,0875	0,12437	0,099989	0,076993	0,12989
4040	2475	0,10145	0,10197	0,083674	0,13189	0,079524	0,081235	0,10917
RON clear		99,1						
MON clear		88,2						
Vapour Pressure		731,74						
Volatilite		985						
%Dist 100°c		49,93						
%Dist 70°c		34,4						

TABLE 1b
Comparison of the result obtained via blending and those of the product obtained

		Weight	Product		1D	1E	1F
			Made	Estimated			
Proximity Index				0,000027526	0,000067452	0,000072577	0,000096807
λ (cm-1)	λ (nm)						
4720	2119	1	0,0021031	0,0021115	0,0021985	0,0020678	0,0020683
4670	2141	1	0,01696	0,016887	0,017029	0,016831	0,016801
4640	2155	1	0,016172	0,016464	0,017171	0,015695	0,016527
4615	2167	1	0,023426	0,022955	0,022671	0,022765	0,023429
4585	2181	1	0,014407	0,014379	0,014241	0,014863	0,014034
4485	2230	1	0,011377	0,011472	0,011516	0,011788	0,011112
4460	2242	1	0,015794	0,015825	0,015718	0,015331	0,016428
4385	2281	1	0,092392	0,090762	0,09071	0,092874	0,088701
4332	2308	1	0,127	0,12402	0,12292	0,1241	0,12505
4305	2323	1	0,10482	0,10678	0,1021	0,10946	0,10879
4260	2347	1	0,10001	0,099412	0,098621	0,095524	0,10409
4210	2375	1	0,065489	0,06726	0,067463	0,066664	0,067653
4170	2398	1	0,063954	0,06449	0,068434	0,064491	0,062546
4135	2418	1	0,066992	0,067348	0,065523	0,067075	0,069445
4105	2438	1	0,066911	0,066281	0,066551	0,064987	0,067336
4060	2463	1	0,10946	0,11196	0,11349	0,11337	0,10903
4040	2475	1	0,10273	0,10157	0,10564	0,10211	0,096959
			Measured standards				
RON clear			99,4	99,2			
MON clear			88,4	88,2			
Vapour Pressure			700	705,0			
Volatility			980	975,0			
%Dist 100°c			58	54,7			
%Dist 70°c			36,8	37			

Example 2

On line control, based on NIR spectra on a mixture of crude oils fed to an atmosphere distillation unit, of yields and properties of the different distillation cuts such as gasoline (38-95°C) benzine (95-149°C) naphtha (149-175°C, jet fuel (175-232°C) light gas oil (232-242°C) heavy gas oil (342-369°C) and atmospheric residue (bp).369°C).

An atmospheric distillation unit in a refinery was fed with a charge 2C which was a mixture in wt% of the following crudes, RUMASHKINO 81%, Iranian Heavy 18%, Iranian light 1%.

Yields of various distillation cuts were desired, the boiling ranges being given above, as well as key properties of each cut as described in Table 2. NIR spectra were measured as in Ex 1 on the crude oil. Min. Index was determined from NIR spectra on standard crude oil (as described above) and was 2.6×10^{-6}. The method of the invention was applied using Procedure 3 and equation 8, in which v was 1, to the bank which was sufficiently dense for 2 standards 2A and 2B to be found with small enough proximity indices. These standards contained (wt%) (for 2A) Romashkino 52% Iranian Heavy 29%. Arabian Heavy 11%, Kuwait 4%, Arabian light 2% and Iranian light 2%) and (for 2B) Iranian Heavy 78%, Romashkino 21% and Arabian Heavy 1%. The data in Table 2 shows the observed properties as well as the yields of the cuts and their properties. The conditions in the distillation unit were maintained in order to keep the 2 standards 2A and 2B as those with small enough proximity indices and hence to keep the properties and yields of the products substantially constant. To double check the process, the properties of standards, estimated (averaged) yields, properties of the products and actual yields were compared, the differences observed being in accordance with standard methods of measurement.

TABLE 2

Determination of yields and properties of cuts from distillation of mixture of crude feed oils

		Weight	Charge 2C			
			Measured	Estimated	2A	2B
	Proximity Index			9,98E-07	1,21E-06	1,33E-06
λ (cm-1)	λ (nm)					
4672	2140,4	1	0,001777942	0,001748627	0,001771733	0,00172552
4640	2155,2	1	0,003139917	0,003211964	0,003256211	0,003167717
4616	2166,4	1	0,00377911	0,003827795	0,003835639	0,003819952
4584	2181,5	1	0,003794844	0,003797791	0,003829737	0,003765845
4484	2230,2	1	0,006094959	0,00614454	0,006272386	0,006016694
4460	2242,2	1	0,009258476	0,009155818	0,009276757	0,009034879
4384	2281	1	0,078089814	0,077898738	0,077667019	0,078130457
4332	2308,4	1	0,15773336	0,157794497	0,157793411	0,157795584
4304	2323,4	1	0,104631107	0,1045241	0,104179066	0,104869135
4260	2347,4	1	0,130690546	0,130249322	0,130445176	0,130053468
4208	2376,4	1	0,087815393	0,087751054	0,087838988	0,08766312
4172	2396,9	1	0,091208037	0,090879399	0,090878774	0,090880025
4132	2420,1	1	0,084648925	0,084706329	0,08465164	0,084761019
4104	2436,6	1	0,0824855	0,082364989	0,082389016	0,082340962
4060	2463,1	1	0,087068028	0,087578898	0,087475	0,087682795
4040	2475,2	1	0,067784043	0,068366138	0,068439449	0,068292827
Density 15°C			0,8663	0,86555	0,8646	0,8665
% Gasoline			7,4	7,4	7,4	7,4
% Benzine			7,6	7,2	7,3	7,2
% Naphta ·			4,3	4,5	4,5	4,5
% Petrol			8,5	8,5	8,6	8,4
% light gas oil LGO			18,9	18,8	19,2	18,5
% Heavy gas oil			4,5	4,5	4,6	4,4
% Residue RAT			49	49,2	48,6	49,8
% Paraffines Naphta			52,2	52,1	53,1	51,2
Flash Point Petrol			59,2	59,5	59,8	59,3
Cloud point LGO			-8,1	-8,1	-8,8	-7,5
% Sulphur RAT			2,8	2,8	2,8	2,9
Viscosity 100°C RAT			53,16	52,72	48,53	56,91

Example 3

Control of an FCC unit from a Feed

The NIR spectrum of the above feed 3D was measured at 4800-4000cm^{-1}, with base line at 4780 cm^{-1}, normalisation of the spectrum and no weighting. The procedure 3 was used with equation 8, with v = 1, and the Min. Index of 2.5 x 10^{-6} the latter having been previously calculated as described above from NIR spectra on standard FCC feeds of known properties.

The cracking unit operated under the following conditions: riser inlet temperature 250°C, riser outlet temperature 525°C, MHSV (Mass Hourly Space Velocity) 78 kg/h per kg, C/O ratio 6.6, activity of catalyst 65 (in Microactivity Test).

The cracking gave a gasoline cut defined by ASTM distillation with initial point of 38°C and 90% distilled at 190°C and a residue defined by ASTM distillation with 10% distilling at 385°C.

By application of Procedure 3 to the bank of samples of FCC feeds 2 standards were found namely 3A, 3B. The cracking process was controlled to keep these 2 standards as those with the smallest proximity indices. To cross check the yields of products were determined experimentally and also estimated by averaging from the standards. The properties and yields estimated as shown in Table 3. The results were all in line with the accuracy based on the reference methods, as well as in line with the properties and yields actually measured.

TABLE 3

Yields and properties of products from FCC reactor						
		Weight	Feed 3D		3A	3B
			. Measured	Estimated		
	Proximity Index			1,10E-06	1,28E-06	1,30E-06
λ (cm-1)	λ (nm)					
4720	2118,6	1	0,00024017	0,000283004	0,000238346	0,000327662
4672	2140,4	1	0,002238801	0,002010364	0,001890879	0,00212985
4640	2155,2	1	0,004237234	0,003903227	0,003874117	0,003932336
4612	2168,3	1	0,005237444	0,004972667	0,004866233	0,005079102
4584	2181,5	1	0,005332797	0,005055095	0,005031089	0,005079102
4484	2230,2	1	0,007970887	0,007756354	0,007744263	0,007768446
4460	2242,2	1	0,011303264	0,011210967	0,011212199	0,011209736
4384	2281	1	0,072994455	0,07273491	0,07292398	0,072545839
4332	2308,4	1	0,152067643	0,152159348	0,151945649	0,152373047
4304	2323,4	1	0,100517606	0,100397569	0,100601923	0,100193214
4260	2347,4	1	0,131209247	0,131514201	0,131487607	0,131540794
4212	2374,2	1	0,091618024	0,091623192	0,091564633	0,091681751
4168	2399,2	1	0,094011773	0,094322962	0,09427582	0,094370104
4132	2420,1	1	0,086184908	0,086675314	0,086678538	0,08667209
4104	2436,6	1	0,081457005	0,081916022	0,081981133	0,081850912
4060	2463,1	1	0,084267922	0,084318052	0,084444043	0,08419206
4040	2475,2	1	0,06911082	0,069146752	0,069239547	0,069053957

Example 4

On line Control of Polybutenes Production

It is desired to control the properties of polybutenes made during their manufacture by adapting immediately the operating conditions to any changes in any product.

They were made by polymerisation of isobutene with an Bronsted acid catalyst to form a crude product from which distillation removes gaseous hydrocarbons and light polymeric products, and leaves heavy polyisobutene.

During the manufacture, the absorbances of heavy polyisobutene (Ref 4A) were measured with an NIR spectrometer in the wavelength region 6000-8850cm^{-1}. The spectrometer had been installed on line in a plant with the aid of a fast side loop situated in the line carrying the heavy polymer remaining after the distillation. An analyser attached to the spectrometer sent within 2 minutes to the controller of the plant a signal relating to the proximity indices with respect to standards.

The method chosen to treat the NIR spectrum involved a discrete selection of wavelengths chosen on the basis of chemical and/or statistical criteria, the chosen wavelengths being between 6079 and 8803cm.$^{-1}$. The absorbances were normalised according to procedure (2).

For a series of standard polyisobutene products, for which the NIR spectra were known, the Minimum Proximity Index was obtained by the method above to be 5x10^{-6}; this Index was not weighted. The proximity indices, between the absorbances of the standards in the bank and those of the unknown from the plant (normalised as above) were calcu-

lated and 5 standards 4B-4F were found with proximity indices < Min. Prox. Index.

The plant was controlled to keep the 5 standards those with the lowest proximity indices. Checking of the process was performed, by averaging the values of each property of those 5 standards in order to calculate the properties for the product namely the viscosity at 100°C, the number average molecular weight (MN), size of the distribution of molecular weights obtained by gel permeation chromatography (called LGPC) as well as the content of butene-1 (BUT-1).

Table 4 shows the results, from which it is clear that the calculated properties (in col 5) were all in agreement with those measured on the unknown by standard methods and were within the limits of reproducibility of those methods for use in the polyisobutene area (on the basis of a 95% probability in any measurement) namely 0.7% for viscosity (ASTM D445), 8.5°C for inflammability point (ASTM D93-80), 5% for number average Molecular Weight and 3% for Molecular Weight distribution (both by Gel Permeation Chromatography), 10% for unsaturation (NMR) and for butene-1 (IR) and 1% for maleinisation index.

Example 5

Control of Production of Low Molecular Weight Polyisobutene

The principles of Example 4 were applied to control the manufacturing unit for production of a low molecular weight polyisobutene (5A). The method adopted was as in Example 4 with the absorbances of the polyisobutene measured as before in the 6000-8850cm^{-1} wavelength range with the aid of the NIR spectrometer installed on the residue line from the distillation unit.

The properties of the product to be kept substantially constant were the viscosity at 100°C, the number average molecular weight, the LGPC (as in Ex.4), the content of butene-1, the inflammability point (IP) and the degree of unsaturation expressed in groups/litre, and the maleinisation index (PIBSA). The unsaturations were of the types VIN, TRI1, TRI2, TRI2cis, TRI2trans, TRITotal and TETRA as defined above. The maleinisation index is particularly important for control of plants to make polyisobutenes as it is of great value to purchasers of low polyisobutenes.

The NIR spectra of a series of standard polyisobutenes whose properties were measured by reference techniques, were determined and from the bank obtained the Minimal Index was determined at 9×10^{-5}, via the unweighted proximity indices. The density of standards in the Bank was sufficiently high for there to be 5 standards 5B-5F inside the sphere with proximity indices with respect to the unknown less than the Minimal Index. The operating process was controlled to keep these 5 standards the ones in the lowest proximity indices. To check, the properties of the product were determined, by averaging the data from these standards. The results are shown in Table 5.1. The properties of the polyisobutene from the plant calculated from the standards were all within the limits of reproducibility of the standard methods. Thus continuously and with total reliability, the quality of product from the plant can thus be obtained and can be maintained taking account of the process dynamics.

TABLE 4
On line Control of the Properties of a High MW Polyisobutene

		Wt	4A		4B	4C	4D	4E	4F
	Prox. Index		Measured	Estimated	2,28E-07	2,41E-07	3,17E-07	4,99E-07	5,05E-07
Wavelength									
λ (cm-1)	λ (nm)								
6079	1645	1	0,034526	0,0345348	0,03445	0,034579	0,034566	0,034566	0,034513
6109	1637	1	0,033387	0,0334816	0,033343	0,033452	0,033511	0,033514	0,033588
6165	1622	1	0,031521	0,0316246	0,031567	0,031568	0,031642	0,031691	0,031655
6200	1613	1	0,029482	0,0295274	0,029529	0,029419	0,029577	0,029578	0,029534
6215	1609	1	0,028092	0,0281402	0,028072	0,028047	0,028148	0,028212	0,028222
6262	1597	1	0,022757	0,0227916	0,022708	0,02274	0,02287	0,022827	0,022813
6418	1558	1	0,009918	0,0099332	0,009884	0,009823	0,010043	0,009945	0,009971
6532	1531	1	0,008198	0,0082184	0,008228	0,008124	0,008355	0,008288	0,008097
6649	1504	1	0,013928	0,0139594	0,013956	0,013878	0,01398	0,014021	0,013962
6698	1493	1	0,018189	0,0181368	0,018174	0,018078	0,018188	0,018186	0,018058
6821	1466	1	0,023312	0,0233096	0,023296	0,023313	0,02329	0,02332	0,023329
6901	1449	1	0,03066	0,03061	0,030665	0,030627	0,030622	0,03062	0,030516
6925	1444	1	0,032947	0,0329416	0,032984	0,032945	0,032842	0,032927	0,03301
6964	1436	1	0,034095	0,0340834	0,034175	0,034129	0,03404	0,034121	0,033952
6998	1429	1	0,033036	0,0330732	0,033113	0,033051	0,033061	0,033057	0,033084
7052	1418	1	0,037285	0,0373202	0,037367	0,037376	0,03725	0,037374	0,037234
7062	1416	1	0,038945	0,0389808	0,039025	0,039019	0,038891	0,038957	0,039012
7092	1410	1	0,042821	0,0429034	0,042882	0,042993	0,042821	0,042866	0,042955
7148	1399	1	0,050224	0,0501864	0,050162	0,050204	0,05023	0,050197	0,050139
7158	1397	1	0,05171	0,0516546	0,051583	0,051672	0,051573	0,051668	0,051777
7199	1389	1	0,055328	0,0552568	0,055321	0,055251	0,055274	0,055195	0,055243
7220	1385	1	0,055837	0,055829	0,055823	0,055857	0,055805	0,055755	0,055905
7231	1383	1	0,05578	0,0557724	0,055758	0,055782	0,055802	0,055606	0,055914
7262	1377	1	0,053775	0,053733	0,053785	0,053713	0,0538	0,053595	0,053772
7294	1371	1	0,048604	0,0484784	0,048495	0,048516	0,048501	0,048403	0,048477
7331	1364	1	0,040558	0,0405078	0,040492	0,040581	0,040499	0,040494	0,040473
7348	1361	1	0,036912	0,0368442	0,036891	0,036937	0,036791	0,036849	0,036753
7375	1356	1	0,028832	0,028823	0,028885	0,028916	0,028736	0,028825	0,028753
7402	1351	1	0,01934	0,0193446	0,019389	0,019411	0,019293	0,019343	0,019287
7899	1266	1	0,002143	0,0020506	0,002127	0,002037	0,002131	0,002039	0,001919
8000	1250	1	0,006563	0,0066608	0,00675	0,006643	0,006601	0,006705	0,006605
8097	1235	1	0,017014	0,0170314	0,016928	0,017022	0,01693	0,017118	0,017159
8197	1220	1	0,033957	0,033925	0,033887	0,033884	0,033837	0,034041	0,033976
8217	1217	1	0,037243	0,0373344	0,037337	0,037276	0,037258	0,037459	0,037342
8251	1212	1	0,043473	0,043491	0,043447	0,043397	0,043469	0,043609	0,043533
8278	1208	1	0,048882	0,0488738	0,048886	0,048835	0,048753	0,049003	0,048892
8333	1200	1	0,080806	0,080871	0,080945	0,080719	0,080878	0,080894	0,080919
8361	1196	1	0,0924	0,0924876	0,092499	0,092582	0,092447	0,092511	0,092399
8375	1194	1	0,091802	0,0918924	0,091893	0,091891	0,091957	0,091803	0,091918
8382	1193	1	0,090957	0,090951	0,090973	0,090952	0,090913	0,090875	0,091042
8403	1190	1	0,088076	0,0879942	0,087981	0,088052	0,0881	0,087893	0,087945
8418	1188	1	0,086503	0,0865104	0,086496	0,086468	0,086638	0,086372	0,086578
8503	1176	1	0,068153	0,0681298	0,068144	0,068087	0,06819	0,068083	0,068145
8540	1171	1	0,058772	0,0587116	0,058757	0,058746	0,058828	0,058655	0,058572
8598	1163	1	0,043961	0,0439804	0,043948	0,043992	0,043996	0,043947	0,044019
8658	1155	1	0,035651	0,0355848	0,035646	0,035571	0,03557	0,035569	0,035568
8703	1149	1	0,031642	0,0315346	0,03152	0,031638	0,031491	0,031545	0,031479
8726	1146	1	0,02824	0,028269	0,028194	0,02837	0,028297	0,028232	0,028252
8803	1136	1	0,013764	0,0137152	0,013641	0,013837	0,013715	0,013645	0,013738
	VISCOSITY		4717	4708,2	4669	4783	5005	4484	4600
	MN		2991	3031,4	3026	3016	3214	2930	2971
	LGPC		1,81	1,812	1,80	1,82	1,78	1,84	1,82
	BUT-1		1,68	1,6298	1,62	1,4	1,669	1,66	1,8

In this Table 1.56E-07 means 1.56×10^{-7}

TABLE 5
On line Control of the Properties of a Polyisobutene of Low Mol. Wt.

		Wt	5A		5B	5C	5D	5E	5F
			Measured	Estimated					
	Prox. Index			4,34E-07	2,28E-07	8,65E-07	9,18E-07	1,07E-06	1,68E-06
Wavelength									
λ (cm-1)	λ (nm)								
6079	1645	1	0,03487	0,0350224	0,034809	0,035165	0,034927	0,03502	0,035191
6109	1637	1	0,033505	0,0336706	0,033428	0,033829	0,033536	0,033725	0,033835
6165	1622	1	0,029642	0,0296054	0,029568	0,029806	0,029475	0,029625	0,029553
6200	1613	1	0,026851	0,02668	0,026667	0,026958	0,026525	0,026706	0,026544
6215	1609	1	0,025316	0,025189	0,025198	0,025414	0,025055	0,025241	0,025087
6262	1597	1	0,020251	0,0201638	0,020177	0,020325	0,020046	0,020202	0,020069
6418	1558	1	0,008942	0,00905	0,009014	0,009098	0,009048	0,009074	0,009016
6532	1531	1	0,007916	0,0080262	0,007969	0,008029	0,008046	0,008052	0,008035
6649	1504	1	0,014038	0,0141226	0,014057	0,014102	0,014121	0,014208	0,014125
6698	1493	1	0,01827	0,0183048	0,018253	0,01832	0,018273	0,018369	0,018309
6821	1466	1	0,023637	0,0236528	0,023648	0,023639	0,023689	0,023643	0,023665
6901	1449	1	0,030691	0,0307184	0,030767	0,030664	0,030755	0,030708	0,030698
6925	1444	1	0,033186	0,0331576	0,033188	0,033115	0,033189	0,033208	0,033088
6964	1436	1	0,035052	0,0350774	0,0351	0,034983	0,035168	0,035051	0,035085
6998	1429	1	0,034516	0,0345532	0,034541	0,034482	0,034606	0,0345	0,034637
7052	1418	1	0,039698	0,0396944	0,039673	0,039522	0,039765	0,039724	0,039788
7062	1416	1	0,041541	0,0415304	0,041504	0,041347	0,041604	0,041588	0,041609
7092	1410	1	0,045553	0,0455686	0,045523	0,045335	0,045654	0,045617	0,045714
7148	1399	1	0,052377	0,052487	0,052493	0,052322	0,052627	0,052425	0,052568
7158	1397	1	0,053934	0,0539828	0,054005	0,053795	0,054148	0,053874	0,054092
7199	1389	1	0,056865	0,0569614	0,05701	0,056767	0,057037	0,056838	0,057155
7220	1385	1	0,056997	0,056996	0,057043	0,056965	0,057052	0,056858	0,057062
7231	1383	1	0,056741	0,0566584	0,056674	0,056626	0,056695	0,056527	0,05677
7262	1377	1	0,053595	0,0535546	0,053611	0,053499	0,053576	0,053515	0,053572
7294	1371	1	0,047392	0,0473396	0,047407	0,047357	0,047322	0,047342	0,04727
7331	1364	1	0,039219	0,039141	0,039245	0,039188	0,039132	0,039186	0,038954
7348	1361	1	0,035369	0,0352522	0,035363	0,03534	0,035213	0,035285	0,03506
7375	1356	1	0,026707	0,026597	0,02671	0,026679	0,02654	0,02663	0,026426
7402	1351	1	0,017328	0,017232	0,017357	0,017328	0,017195	0,017258	0,017022
7899	1266	1	0,002464	0,0024384	0,00244	0,002455	0,002472	0,002381	0,002444
8000	1250	1	0,007208	0,007183	0,00719	0,00714	0,007244	0,007126	0,007215
8097	1235	1	0,017338	0,0172718	0,017276	0,01724	0,017281	0,017216	0,017346
8197	1220	1	0,035357	0,0352078	0,035245	0,035151	0,035316	0,034991	0,035336
8217	1217	1	0,039433	0,0393774	0,039449	0,039195	0,03959	0,039126	0,039527
8251	1212	1	0,047005	0,0468886	0,046848	0,046753	0,047075	0,046638	0,047129
8278	1208	1	0,05312	0,0530672	0,053062	0,052878	0,053291	0,052931	0,053174
8333	1200	1	0,081058	0,0809726	0,081013	0,080977	0,080954	0,081039	0,08088
8361	1196	1	0,093478	0,093531	0,093501	0,093565	0,093469	0,093651	0,093469
8375	1194	1	0,094014	0,0941538	0,094091	0,094159	0,09414	0,094226	0,094153
8382	1193	1	0,093212	0,09345	0,093337	0,093337	0,093457	0,093559	0,09356
8403	1190	1	0,08976	0,0899258	0,089806	0,089808	0,089953	0,089966	0,090096
8418	1188	1	0,08678	0,0869858	0,086901	0,086907	0,086959	0,087037	0,087125
8503	1176	1	0,06419	0,0641896	0,064217	0,064345	0,064015	0,064341	0,06403

TABLE 5 (cont)
On line Control of the Properties of a Polyisobutene of Low Mol. Wt.

		Wt	5A		5B	5C	5D	5E	5F
			Measured	Estimated					
	Prox. Index			4,34E-07	2,28E-07	8,65E-07	9,18E-07	1,07E-06	1,68E-06
Wavelength									
λ (cm-1)	λ (nm)								
8540	1171	1	0,054912	0,0548696	0,054942	0,055027	0,054736	0,055017	0,054626
8598	1163	1	0,040824	0,0408046	0,04087	0,040884	0,040724	0,040918	0,040627
8658	1155	1	0,03355	0,0335614	0,033553	0,033718	0,033461	0,033613	0,033462
8703	1149	1	0,029161	0,0291404	0,029156	0,029278	0,029022	0,029172	0,029074
8726	1146	1	0,025375	0,025314	0,025338	0,02541	0,025223	0,025394	0,025205
8803	1136	1	0,011761	0,0116668	0,011764	0,011772	0,011618	0,011658	0,011522
	Viscosity		225	224,6	221	237	213	209	243
	MN		946	923	926	930	914	902	943
	LGPC		1,59	1,594	1,58	1,63	1,55	1,62	1,59
	VIN		0,02	0,0216	0,017	0,025	0,018	0,021	0,027
	TRI1		0,012	0,0112	0,01	0,009	0,01	0,017	0,01
	TRI2		0,41	0,407	0,411	0,405	0,425	0,414	0,38
	TRI2c		0,112	0,1156	0,115	0,111	0,121	0,121	0,11
	TRI2t		0,298	0,2914	0,296	0,294	0,304	0,293	0,27
	TRItot		0,578	0,5766	0,586	0,557	0,594	0,598	0,548
	TETRA		0,163	0,1686	0,159	0,177	0,17	0,17	0,167
	BUT-1		7,0	7,3	7,2	7,2	7,5	7,13	7,47
	Flash Point		171	170	170	172	168	165	175
	PIBSA		99	99,2	99,5	98,6	98,4	99,3	100,1

TABLE 6
Manufacture of a Polyethylene

		Wt	6A		6B	6C	6D	6E	6F
			Measured	Estimated					
	Prox. Index			0,0042626	0,0072895	0,0095186	0,012812	0,017956	0,020326
Wavelength									
λ (cm-1)	λ (nm)								
5520	1812	1	2,9479	2,96034	2,9491	2,9576	2,9467	2,99	2,9583
5532	1808	1	2,9677	2,98038	2,9708	2,978	2,9663	3,0081	2,9787
5544	1804	1	2,9663	2,97482	2,9668	2,9721	2,96	3,0018	2,9734
5556	1800	1	2,9003	2,90612	2,898	2,9034	2,891	2,9307	2,9075
5568	1796	1	2,7954	2,8019	2,7949	2,7982	2,7872	2,8221	2,8071
5580	1792	1	2,7574	2,76272	2,7576	2,7579	2,7484	2,7806	2,7691
5592	1788	1	2,8275	2,83096	2,827	2,8257	2,8166	2,848	2,8375
5604	1784	1	2,9641	2,96714	2,9628	2,9637	2,9534	2,9834	2,9724
5616	1781	1	3,1253	3,12946	3,1245	3,1266	3,1188	3,1432	3,1342
5628	1777	1	3,4014	3,40732	3,4035	3,4037	3,3982	3,4176	3,4136
5640	1773	1	3,9219	3,9267	3,9225	3,9257	3,9216	3,8356	3,9281
5700	1754	1	3,271	3,2721	3,2677	3,2734	3,2756	3,2707	3,2731
5712	1751	1	3,5186	3,5218	3,5101	3,5287	3,5403	3,519	3,5109
5724	1747	1	3,967	3,9723	3,958	3,9822	3,9968	3,9724	3,9521
5736	1743	1	4,5291	4,5327	4,5232	4,5424	4,5574	4,5313	4,5092
5748	1740	1	5,4361	5,431	5,4283	5,4432	5,4697	5,4195	5,3943
5760	1736	1	6,2954	6,28316	6,2855	6,2961	6,3339	6,274	6,2263
5772	1733	1	6,1311	6,11846	6,1275	6,1305	6,1556	6,1092	6,0695
5784	1729	1	5,3685	5,36016	5,3687	5,3736	5,3895	5,3388	5,3302
5796	1725	1	4,7353	4,73128	4,7371	4,7434	4,7547	4,7058	4,7154
5808	1722	1	4,2184	4,21624	4,2189	4,22	4,2259	4,1997	4,2167
5820	1718	1	3,7382	3,7354	3,7383	3,7317	3,7329	3,7265	3,7476
5832	1715	1	3,2482	3,24516	3,252	3,2379	3,2325	3,2378	3,2656
5844	1711	1	2,7005	2,69712	2,7088	2,6865	2,6767	2,6865	2,7271
5856	1708	1	2,1677	2,16416	2,1782	2,1539	2,1453	2,1464	2,197
5868	1704	1	1,7811	1,777	1,7899	1,7685	1,7611	1,7578	1,8077
5880	1701	1	1,543	1,53756	1,549	1,5317	1,5247	1,5187	1,5637

TABLE 6 (cont)
Manufacture of a Polyethylene

		Wt	6A		6B	6C	6D	6E	6F
			Measured	Estimated					
	Prox. Index			0,0042626	0,0072895	0,0095186	0,012812	0,017956	0,020326
Wavelength									
λ (cm-1)	λ (nm)								
5892	1697	1	1,386	1,37964	1,3902	1,3751	1,3678	1,362	1,4031
5904	1694	1	1,2531	1,24688	1,256	1,2422	1,2334	1,2363	1,2665
5916	1690	1	1,1365	1,1301	1,135	1,1265	1,1181	1,1269	1,144
8040	1244	1	2,017	2,00228	2,007	1,9968	1,9988	2,0068	2,002
8052	1242	1	2,1798	2,16904	2,1741	2,1633	2,1689	2,1757	2,1632
8064	1240	1	2,3554	2,3495	2,3502	2,3435	2,3506	2,3583	2,3449
8076	1238	1	2,5542	2,54602	2,5463	2,5412	2,5411	2,5583	2,5432
8088	1236	1	2,77	2,7631	2,764	2,7595	2,7549	2,778	2,7591
8100	1235	1	3,0086	3,00852	3,006	3,01	3,0001	3,0222	3,0043
8112	1233	1	3,2815	3,28462	3,281	3,2858	3,2755	3,2932	3,2876
8124	1231	1	3,5883	3,59138	3,5901	3,5889	3,5827	3,5958	3,5994
8136	1229	1	3,9312	3,932	3,9335	3,9321	3,9259	3,9335	3,935
8148	1227	1	4,3057	4,30886	4,3138	4,3117	4,3029	4,3088	4,3071
8160	1225	1	4,6904	4,70348	4,7083	4,7085	4,6972	4,7021	4,7013
8172	1224	1	5,0567	5,0748	5,0806	5,085	5,0706	5,0702	5,0676
8184	1222	1	5,3584	5,37704	5,3885	5,3897	5,3754	5,3703	5,3613
8196	1220	1	5,5454	5,56502	5,5766	5,5765	5,5653	5,5602	5,5465
8208	1218	1	5,5949	5,61744	5,6243	5,6316	5,6174	5,6161	5,5978
8304	1204	1	3,9622	3,97292	3,9776	3,9785	3,9684	3,9677	3,9744
8316	1203	1	3,7097	3,71178	3,7158	3,7128	3,7071	3,7087	3,7145
8328	1201	1	3,452	3,44774	3,4551	3,4456	3,4421	3,445	3,4509
8340	1199	1	3,1855	3,18512	3,1931	3,1844	3,1794	3,1793	3,1894
8352	1197	1	2,9428	2,94286	2,9445	2,9422	2,9419	2,9321	2,9536
8364	1196	1	2,7439	2,74022	2,7361	2,7369	2,7463	2,727	2,7548
8376	1194	1	2,6033	2,60352	2,5999	2,603	2,6104	2,5913	2,613
8388	1192	1	2,5465	2,55012	2,5457	2,553	2,5529	2,5426	2,5564
8400	1190	1	2,54	2,53978	2,5322	2,5348	2,5421	2,5409	2,5489
8412	1189	1	2,4926	2,48966	2,4825	2,4746	2,4951	2,497	2,4991
8424	1187	1	2,3635	2,35776	2,3517	2,343	2,3666	2,3639	2,3636
8436	1185	1	2,1984	2,1897	2,1797	2,1783	2,2041	2,1911	2,1853
8448	1184	1	2,047	2,03806	2,0245	2,0367	2,0514	2,0337	2,044
8460	1182	1	1,9027	1,89284	1,8818	1,8996	1,9027	1,8872	1,8929
8472	1180	1	1,7662	1,75796	1,7562	1,7615	1,7655	1,7557	1,7509
8484	1179	1	1,6745	1,66826	1,6685	1,6682	1,6732	1,6694	1,662
8496	1177	1	1,6317	1,61862	1,6109	1,6228	1,6257	1,618	1,6157
grade			4,4	4,3	4,2	4,4	4,1	4,3	4,6
density			0,953	0,952	0,952	0,953	0,952	0,952	0,951

Example 6

Control of Manufacture of a Polyethylene

Ethylene was polymerised with a chromium catalyst in a plant to produce polyethylene, whose properties of density and fluidity index/Melt Index (measured according to the IF2 standard method) (called grade) were to control its market specification. The product 6A, in the form of a powder, required rapid measurement of these properties to correct the plant operating conditions to ensure manufacture of a polymer of constant quality.

The NIR spectra of a series of standard polyethylenes were determined by means of a Fourier Transform NIR spectrometer in the 5500-8400cm^{-1} region, as well as their densities and fluidity indices to obtain a bank of standards. The absorbances of the spectra were normalised as described above, to ensure better known numerical stability for the data. The Minimal Proximity Index was calculated from the unweighted proximity indices of the standards (according to Eq.2) and by means of the technique of Eq.8 in which v was 1.1, the proximity index to the product 6A was chosen at 0.025.

The proximity indices between the unknown polyethylene 6A from the plant and the standards were calculated according to Eq.2, and three standards 6B, 6C and 6D were found with small enough proximity indices. The polymerisation process was controlled to keep these 3 standards as those with the smallest proximity indices and hence to keep the properties of the product substantially constant. To check, the properties of standards 6B-D were averaged to give

the properties of the unknown product 6A in less than 1 minute, demonstrating immediate reaction to all variations in the production operation. The results are shown in Table 6, and are in perfect agreement with the properties determined by reference methods, and within their reproducibilities, namely 1‰ for density and 14% for grade.

The method may be applied in the same way to the determination of other properties, for example percentage of comonomer in an ethylene copolymerisation, the degree of conversion of the reaction or the content of volatiles, as well as to other types of polymerisations to polyethylene such as ones with Ziegler Natta catalysts.

Example 7

Controlling Production of a Polyethylene Glycol

A polyalkoxylenated product had been made discontinuously by polymerisation in the liquid phase of one or more epoxides specifically ethylene oxide with an organic compound possessing at least one active hydrogen atom, such as an alcohol specifically butanol. The values of the properties of the product during the process had hitherto been regularly evaluated in the laboratory by standard methods during the production in order to determine the necessary amounts of epoxide. However, the times to obtain the analytical results were generally prohibitive in terms of the amounts of epoxide consumed and quality of product obtained during non optimum operations.

The method of the present invention was applied to this process. A band of standards for polyethylenoxylated butanols covering the field between low ones (Mol. Wt about 200) up to high ones (Mol. Wt. of the order of 9000) was generated incorporating the properties of a number of these compounds as well as their spectra, determined in the 4000-8400cm^{-1} wavelength region with an FT NIR spectrometer. The properties considered were the hydroxyl index (fundamental for the conduct/progress of the reaction) as well as the viscosity measured at 100°C and the molecular weight.

The bank of data was applied by the method of the invention to the production of a polyethylenoxylated butanol of Molecular Weight of about 8000 (PEG 8000). From the standards with spectra normalised per Eq.3 the Minimal Index was calculated at 1.2x10^{-4}. The Proximity Indices between the unknown PEG 8000 and the standards were calculated (using Eq. 2) and four standards 7A, 7B, 7C and 7D and 7E were found with Proximity Index values less than the Minimal Index. The process was controlled to keep these 4 standards those with proximity indices less than the Minimal Index and hece maintain the properties of the product. To check this, the properties of the unknown PEG 8000 were calculated by averaging the properties of the standards with (as shown in Table 7) excellent results for all which were obtained in less than 1 minute, showing the maintenance or immediate correction of the level of ethylene oxide used in order to maintain the final quality of the products. Furthermore the differences obtained between the results obtained by the above calculations and by standard methods were all inside the limits of reproducibility of those reference methods, namely 0.7% for the viscosity (by ASTM D445) and 5.8% and 3.6% respectively for the hydroxyl index below and above 100 (ASTM D4274). The Molecular Weight was obtained directly from the hydroxyl index with the same reproducibility values.

TABLE 7

Control of a Production Unit for PEG								
		Wt	7A		7B	7C	7D	7E
			Measured	Estimated				
	Prox. Index			0,00006519	0,00000977	0,00007494	0,00010457	0,00011574
Wavelength								
λ (cm^{-1})	λ (nm)							
4164	2402	1	0,12662	0,121605	0,12559	0,1212	0,12117	0,11846
4308	2321	1	0,24254	0,2387275	0,24285	0,23781	0,23696	0,23729
4524	2210	1	0,054854	0,0567045	0,054802	0,056171	0,057599	0,058246
4836	2068	1	0,048031	0,0485855	0,048451	0,048238	0,048588	0,049065
5172	1933	1	0,059102	0,06188575	0,061585	0,061986	0,064102	0,05987
5436	1840	1	0,056088	0,0555625	0,056049	0,0555	0,055054	0,055647
5544	1804	1	0,068293	0,06745175	0,067773	0,066995	0,067073	0,067966
5748	1740	1	0,10824	0,107665	0,10872	0,10703	0,10673	0,10818
5856	1708	1	0,037196	0,0374255	0,037003	0,037603	0,037295	0,037801
6624	1510	1	0,014687	0,015498	0,014728	0,016063	0,01551	0,015691
6684	1496	1	0,019234	0,01960475	0,019068	0,019792	0,019826	0,019733
6720	1488	1	0,020139	0,02084475	0,020349	0,021013	0,020942	0,021075
6792	1472	1	0,022751	0,023453	0,022848	0,023636	0,023758	0,02357
6972	1434	1	0,030389	0,03078325	0,030175	0,030929	0,03119	0,030839
7092	1410	1	0,021148	0,02166525	0,021221	0,022095	0,021621	0,021724
7116	1405	1	0,021822	0,02246175	0,02158	0,022824	0,02273	0,022713
7920	1263	1	0,004193	0,00522035	0,0042156	0,0057718	0,0054551	0,0054389
8172	1224	1	0,03318	0,0330015	0,032074	0,032927	0,032945	0,03406
8352	1197	1	0,011492	0,0118575	0,010926	0,012427	0,011449	0,012628
Hydroxyl Index			13,1	13,1	13,1	13	13,2	13,15
Viscosity			701	704	703	710	708	695
Molec. Weight			8560	8612,5	8400	8370	8450	9230

Example 8

Control of Production of a Process Oil

The NIR spectrum between 4800 and 4000cm^{-1} with normalisation of the absorbances, [the base line being taken at 4780cm^{-1}] was measured on a process Oil Reference 8D of "Enerthene" type which was made by a process of mixing a neutral base oil and aromatic-containing vacuum distillate extract. From a bank of standard process oils of this type, Minimal Index was found by the Minimal Index Procedure to be $5x10^{-7}$, providing a sphere of identity. 3 standard oils 8A, 8B and 8C were found with proximity indices with respect to 8D less than the Minimal Index and hence inside that sphere. The properties of oils 8A, 8B, 8C and their spectra and the spectrum of 8D are given in Table 8. The mixing process was performed to keep those standards the ones with lowest proximity indices with respect to the product oil, and hence maintain its properties. This was checked by arithmetic mean averaging of the properties of 8A, 8B and 8C,

to estimate the properties of 8D, and these together with the measured properties of 8D are given also in Table 8.

The single analysis gave all the properties without regression calculation and with an accuracy in line with the reproducibility of the reference methods.

In Table 8, the expression 4.20 E-04 means 4.2×10^{-4} and PCA means Polycyclic Aromatic hydrocarbon.

TABLE 8 - Process oil production

	Loading	Oil D Measured	Oil D Estimated	Oil 8A	Oil 8B	Oil 8C
Proximity Index			1.09×10^{-7}	3.5×10^{-7}	1.19×10^{-7}	2.19×10^{-7}
Wavelength						
λ (cm-1) λ (nm)						
4700 2127	1	4,2000000E-04	3,5000000E-04	3,2000000E-04	3,5000000E-04	3,8000000E-04
4888 2133	1	7,3000000E-04	6,4866667E-04	6,1000000E-04	6,7000000E-04	8,6000000E-04
4680 2136	1	9,8000000E-04	9,6333333E-04	9,6000000E-04	9,4000000E-04	8,9000000E-04
4664 2144	1	1,8300000E-03	1,7833333E-03	1,7600000E-03	1,7600000E-03	1,8300000E-03
4656 2147	1	2,1600000E-03	2,0900000E-03	2,0900000E-03	2,0600000E-03	2,1200000E-03
4648 2151	1	2,5100000E-03	2,4300000E-03	2,4100000E-03	2,4100000E-03	2,4700000E-03
4632 2158	1	2,9500000E-03	2,9233333E-03	2,8600000E-03	2,9100000E-03	3,0000000E-03
4624 2162	1	3,1100000E-03	3,0966667E-03	3,0100000E-03	3,0800000E-03	3,2000000E-03
4616 2166	1	3,1700000E-03	3,1833333E-03	3,1200000E-03	3,1800000E-03	3,2500000E-03
4600 2173	1	3,1000000E-03	3,1466667E-03	3,1100000E-03	3,1600000E-03	3,1700000E-03
4592 2177	1	3,0700000E-03	3,0500000E-03	3,0000000E-03	3,0500000E-03	3,1000000E-03
4576 2185	1	2,8300000E-03	2,6800000E-03	2,6500000E-03	2,6800000E-03	2,8100000E-03
4568 2189	1	2,3200000E-03	2,3133333E-03	2,2500000E-03	2,3100000E-03	2,3800000E-03
4560 2192	1	2,2300000E-03	2,1933333E-03	2,1500000E-03	2,1600000E-03	2,2700000E-03
4540 2202	1	2,0200000E-03	1,9966667E-03	2,0000000E-03	1,9800000E-03	2,0100000E-03
4504 2220	1	2,3400000E-03	2,3133333E-03	2,2900000E-03	2,2900000E-03	2,3600000E-03
4472 2236	1	3,2300000E-03	3,2000000E-03	3,1600000E-03	3,1900000E-03	3,2600000E-03
4440 2252	1	6,1400000E-03	6,0966667E-03	6,0800000E-03	6,0600000E-03	6,1500000E-03
4432 2256	1	7,8000000E-03	7,8100000E-03	7,7800000E-03	7,7700000E-03	7,8800000E-03
4424 2260	1	1,0270000E-02	1,0210000E-02	1,0180000E-02	1,0190000E-02	1,0260000E-02
4416 2264	1	1,3160000E-02	1,3130000E-02	1,3100000E-02	1,3090000E-02	1,3200000E-02
4408 2268	1	1,6510000E-02	1,6490000E-02	1,6430000E-02	1,6470000E-02	1,6570000E-02
4400 2272	1	1,9410000E-02	1,9386667E-02	1,9340000E-02	1,9350000E-02	1,9470000E-02
4392 2276	1	2,0970000E-02	2,0963333E-02	2,0930000E-02	2,0940000E-02	2,1020000E-02
4382 2282	1	2,1900000E-02	2,1913333E-02	2,1870000E-02	2,1930000E-02	2,1940000E-02
4376 2285	1	2,2570000E-02	2,2530000E-02	2,2510000E-02	2,2620000E-02	2,2660000E-02
4368 2289	1	2,3080000E-02	2,3053333E-02	2,3030000E-02	2,3030000E-02	2,3100000E-02
4352 2297	1	2,8240000E-02	2,8183333E-02	2,8170000E-02	2,8160000E-02	2,8220000E-02
4344 2302	1	3,3140000E-02	3,3196667E-02	3;3230000E-02	3,3220000E-02	3,3140000E-02
4330 2309	1	3,8690000E-02	3,8760000E-02	3,8850000E-02	3,8810000E-02	3,8680000E-02
4320 2314	1	3,4290000E-02	3,4320000E-02	3,4380000E-02	3,4300000E-02	3,4300000E-02
4312 2319	1	2,0890000E-02	3,0883333E-02	3,0830000E-02	3,0870000E-02	3,0950000E-02
4304 2323	1	2,8580000E-02	2,8576667E-02	2,8660000E-02	2,8560000E-02	2,8610000E-02
4296 2327	1	2,6340000E-02	2,6386667E-02	2,6340000E-02	2,6400000E-02	2,6420000E-02
4280 2331	1	2,5250000E-02	2,5223333E-02	2,5200000E-02	2,5230000E-02	2,5240000E-02
4280 2336	1	2,5780000E-02	2,5766667E-02	2,5800000E-02	2,5780000E-02	2,5780000E-02
4272 2340	1	2,8200000E-02	2,8263333E-02	2,8300000E-02	2,8290000E-02	2,8200000E-02
4258 2348	1	3,2280000E-02	3,2410000E-02	3,2500000E-02	3,2470000E-02	3,2260000E-02
4248 2354	1	3,9760000E-02	2,9810000E-02	2,9870000E-02	2,9820000E-02	2,9740000E-02
4240 2358	1	2,7120000E-02	2,7133333E-02	2,7120000E-02	2,7170000E-02	2,7110000E-02
4232 2362	1	2,5410000E-02	2,5393333E-02	2,5410000E-02	2,5410000E-02	2,5360000E-02
4224 2367	1	2,3930000E-02	2,4000000E-02	2,4000000E-02	2,4020000E-02	2,3980000E-02

TABLE 8 (cont)
Process oil production

	Loading	Oil D Measured	Oil D Estimated	Oil 8A	Oil 8B	Oil 8C
Proximity Index			1.09×10^{-7}	3.5×10^{-7}	1.19×10^{-7}	2.19×10^{-7}
λ (cm-1) λ (nm)						
4212 2374	1	2,2630000E-02	2,2630000E-02	2,2680000E-02	2,2650000E-02	2,2560000E-02
4200 2380	1	2,2060000E-02	2,2106667E-02	2,2140000E-02	2,2160000E-02	2,2020000E-02
4192 2385	1	2,2010000E-02	2,2043333E-02	2,2110000E-02	2,2070000E-02	2,1950000E-02
4184 2390	1	2,2220000E-02	2,2226667E-02	2,2310000E-02	2,2230000E-02	2,2140000E-02
4176 2394	1	2,2780000E-02	2,2816667E-02	2,2860000E-02	2,2840000E-02	2,2750000E-02
4170 2398	1	2,3160000E-02	2,3213333E-02	2,3290000E-02	2,3210000E-02	2,3140000E-02
4160 2403	1	2,2840000E-02	2,2850000E-02	2,2890000E-02	2,2860000E-02	2,2800000E-02
4152 2408	1	2,1810000E-02	2,1843333E-02	2,1900000E-02	2,1860000E-02	2,1770000E-02
4136 2417	1	2,0630000E-02	2,0630000E-02	2,0700000E-02	2,0640000E-02	2,0550000E-02
4120 2427	1	2,0170000E-02	2,0186667E-02	2,0240000E-02	2,0220000E-02	2,0100000E-02
4104 2436	1	1,9520000E-02	1,9563333E-02	1,9590000E-02	1,9590000E-02	1,9510000E-02
4092 2443	1	1,9530000E-02	1,9593333E-02	1,9640000E-02	1,9610000E-02	1,9530000E-02
4080 2450	1	2,1540000E-02	2,1513333E-02	2,1550000E-02	2,1530000E-02	2,1460000E-02
4072 2455	1	2,3530000E-02	2,3530000E-02	2,3550000E-02	2,3530000E-02	2,3510000E-02
4068 2458	1	2,3430000E-02	2,3443333E-02	2,3460000E-02	2,3450000E-02	2,3420000E-02
4048 2470	1	1,8990000E-02	1,9010000E-02	2,9050000E-02	1,9020000E-02	1,8960000E-02
4000 2500	1	1,4630000E-02	1,4593333E-02	1,4620000E-02	1,4580000E-02	1,4580000E-02
Density kg/l		0,9348	0,9351	0,9350	0,9345	0,9360
Sulphur %		2,25	2,28	2,37	1,98	2,51
PCA %		2.60	2.57	2.88	2.74	2.1
Viscosity at 100°C sCt		33,19	33,22	33,23	32,25	34,18
Flash Point Cleveland °C		310	311	310	308	315

Claims

1. Method of controlling a process for which a material X is a feed or a product, in order to keep substantially constant the value V_c of a property P of said product or the product of said process from said feed, or the yield of said process, which method comprises measuring the absorption D_{ix} of said material at more than one wavelength in the region 600-2600nm, comparing signals (i) indicative of said absorptions or a mathematical function thereof with signals (ii) indicative of absorptions D_{im} at the same wavelengths or a mathematical function thereof for at least 2 standards S_m for which the said property or yield has a known value V, at least one of said standards S_{mc} having a value V_c for said property or yield and controlling said process to ensure that said standard S_{mc} or standard(s) S_{mc} is the standard or standards having the smaller or smallest average value of the absolute difference at each wavelength i between the signal for said material and the signal from the standard S_m.

2. A method according to claim 1 which comprises comparing signals (i) from said material with signals (ii) from standards S_m, at least 2 of which have smallest average values of the differences, and the average of the values V of the property or yield of said at least 2 standards being V_c.

3. A method according to claim 1 or 2 comprising comparing absorptions D_ix (or a derivative thereof) with absorption D_im or a derivative thereof.

4. A method according to any one of claims 1-3 wherein the standard S_{mc} is such that in relation to the material X and the or each standard S_{mc} the following function is met

$$\frac{i_{xm}}{\Sigma D_{ix}} < \text{experimental error}$$

wherein i_{xm} is the proximity index and is defined by $i^2(xm) = \Sigma(D_{ix}-D_{im})^2$ and the experimental error is in determining said property or yield in the standard, and in the case where more than one standard S_{mc} meets the function, averaging the properties or yields from said standards gives a value V_c.

5. A modification of a method according to claim 4 wherein the comparison of signals (i) is with signals (ii) indicative of absorptions D_{im} at the same wavelength or a mathematical function thereof of one standard S_{mc} having the known value V_c of said proeprty or yield and controlling said process to ensure that the function specified in claim 4 is met.

6. A method according to claim 4 or 5 wherein the proximity index is less than the minimal index i_m which has been determined from the standards Sa, Sb, Sc ...... by (a) calculating for each pair of standards Sa/Sb, Sa/Sc the value of $i^2(a,b)$ etc, (b) relating the values of $i^2(a,b)$ etc to the corresponding differences EP (ab) in properties Pa, Pb etc (c) calculating for each value L for which $i^2(ab)$ is $\leq L$, the average of the corresponding differences EPab, (d) calculating Minimal index from the value of minimal index $i^2(ab)$ where average EPab is the same as reproducibility standard for the property.

7. A method according to any one of the preceding claims wherein the process is controlled in a closed loop control system to control the processing equipment in relation to a process for which the material X is a product.

8. A method according to any one of the preceding claims wherein said process is a hydrocarbon conversion or separation process, preferably a reforming or catalytic cracking or hydrotreatment, or distillation or blending.

9. A method according to any one of claims 1-7 wherein said process is at least one of a polymerization, an oligomerization or an organic reaction in which at least one of the reactant and a product is a functionalized compound.

10. A method according to any one of claims 1-7 wherein said material X is a composition comprising part of a lubricating oil fraction obtainable from a vacuum distillation of oil.

FIG.1

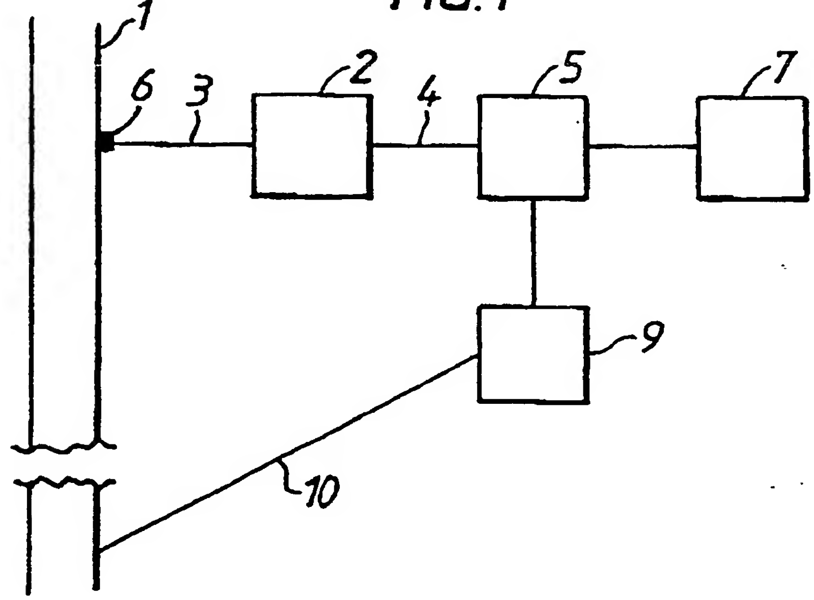
1
6
3
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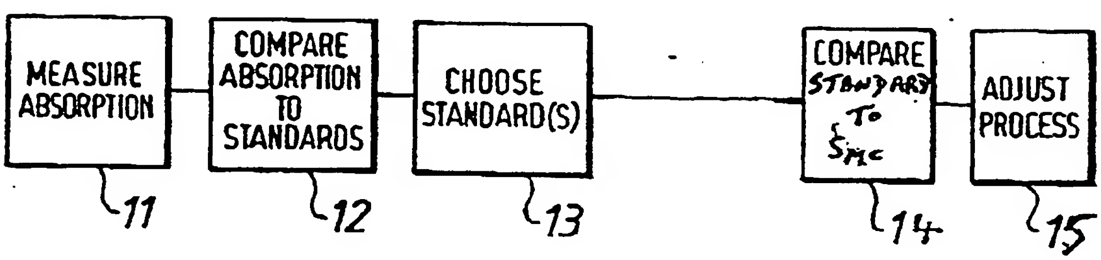
FIG.2


MEASURE ABSORPTION
COMPARE ABSORPTION TO STANDARDS
CHOOSE STANDARD(S)
COMPARE STANDARD TO SMC
ADJUST PROCESS
11
12
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14
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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 43 0003

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US-A-5 023 804 (PERKIN-ELMER) * column 1, line 31 - line 39 * * column 3, line 39 - column 4, line 9 * ---	1,3,8,10	G01N21/35
Y	US-A-5 361 912 (KRIEG) * abstract * * column 4, line 26 - line 29 * ---	1,3,8,10	
D,Y	EP-A-0 345 182 (NAPHTACHIMIE) * abstract * ---	8,10	
A	US-A-4 882 755 (YAMADA) * column 1, line 39 - line 58 * * column 4, line 46 - line 68 * ---	1	
A	US-A-5 153 140 (LANGFELD) * abstract * * column 4, line 34 - line 48 * ---	1	
A	EP-A-0 437 829 (HEWLETT PACKARD) * abstract * * page 5, line 29 - line 55 * * page 9, line 33 - line 45 * * figures 3,4 * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G01N
A	EP-A-0 625 702 (FOXBORO) * abstract * * column 6, line 41 - line 53 * * column 7, line 4 - line 25 * * figure 5 * ---	1	
A	EP-A-0 607 048 (TOA) * abstract * * page 3, line 12 - line 18 * * page 3, line 55 - page 4, line 44 * * figures 1-5 * --- -/--	1,3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 September 1996	Thomas, R.M.

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Application Number
EP 96 43 0003

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 631 810 (PFIZER) * abstract * * column 7, line 35 - line 53 * * column 12, line 39 - column 13, line 13 * * column 14, line 25 - line 27 * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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